Biosolids-Derived Biochar for Micropollutant Removal from Wastewater

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BIOSOLIDS-DERIVED BIOCHAR FOR MICROPOLLUTANT REMOVAL FROM WASTEWATER

by

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ABSTRACT
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Trace organic compounds including antibiotics, hormones, pharmaceuticals and personal care products are discharged to the environment with liquid and solid effluent streams from water resource recovery facilities. These compounds are referred to as micropollutants, and can have negative impacts in receiving waters. Current wastewater treatment processes are not specifically designed to remove micropollutants, and many of these compounds are recalcitrant to conventional treatment technologies. Triclosan (TCS) was selected as a representative micropollutant in this study due to frequent detection in liquid effluents, residual biosolids, and surface waters. Pyrolysis - the thermochemical decomposition of organic matter at elevated temperatures in the absence of oxygen - of wastewater biosolids is an emerging sludge management technique that can produce energetic by-products including biochar, py-oil, and py-gas. Biosolids-derived biochar is a carbon-rich material that is growing in popularity due to its beneficial use as a soil amendment and adsorbent. The objective of this research was to determine if biosolids-derived biochar could be implemented in flow-through columns as a polishing step at the end of wastewater treatment to remove micropollutants. Column adsorption experiments were conducted to determine the impact of pH, flow rate, organic micropollutants, inorganic nutrients, and secondary wastewater effluent on the removal of TCS via biosolids-derived biochar adsorbents. Results demonstrated that changes in pH from 7 to 8.5 do not affect TCS removal. Increased removal of TCS was observed at lower flow rates (2.6 gpm/ft^2) compared to higher flow rates (10.3 gpm/ft^2), presumably due to shorter empty bed contact time. Inorganic nutrients, ammonium and phosphate, decreased triclosan adsorption to biochar. Also, the presence of the organic micropollutants 17β-estradiol and sulfamethoxazole in solution decreased the adsorption of triclosan to biochar. In wastewater, triclosan was efficiently removed by adsorption biosolids-derived biochar, but exhibited decreased removal rates and adsorption capacity due to the presence of organic matter relative to Milli-Q water. Column adsorption experiments with commercial adsorbents were conducted to compare triclosan removal with biosolids-derived biochar. Activated carbon (CF300-AC) demonstrated higher adsorption capacity for triclosan compared to biosolids-derived biochar, but biosolids-derived biochar was superior to the pine-wood biochar (BN-biochar). This study demonstrated that biosolids-derived biochar can remove triclosan from water and wastewater in continuous flow-through columns, and could be implemented as a tertiary treatment technology to remove micropollutants. Future pilot-scale studies should be conducted with biosolids-derived biochar adsorbents to determine the overall feasibility of implementing biochar filtration processes at water resource recovery facilities.

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DEDICATION

I would like to dedicate this thesis to my family in Clinton, KY. I wouldn't be where I am today without your encouragement and continual support of my academic pursuits. I would also like to thank my friends and Amanda for their support and encouragement throughout this project.

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1 INTRODUCTION

1.1 Motivation

Micropollutants are trace organic compounds that are ubiquitous in the natural environment as a result of increasing anthropogenic activity (Blair et al. 2013; Kolpin and Meyer 2002). Micropollutants include a broad range of organic compounds detected at µg/L or lower concentrations including pharmaceuticals, antimicrobials, hormones, and more. Concern has risen regarding the presence of micropollutants in water bodies due to their potential adverse impacts on environmental and public health (Kidd et al. 2007; Pal et al. 2014). Many micropollutants are not currently regulated under federal law and water resource recovery facilities (WRRFs) are not specifically designed to remove these compounds, thus WRRFs are continuously discharging micropollutants into receiving water bodies. Even though these compounds are commonly found at low concentrations, they can have negative environmental effects, which has promoted interest in developing sustainable treatment technologies capable of removing micropollutants prior to being discharged to the environment, including removal by adsorption.

Biosolids are a carbon-rich residual solid product generated from municipal WRRFs, and represent a concentrated carbon source that could be readily transformed into an adsorbent. Approximately half of biosolids in the US are reused as a soil amendment, but other biosolids are landfilled or incinerated (Kinney et al. 2008; McNamara et al. 2016). Pyrolysis is an emerging biosolids management technology that captures energy from organic compounds such as biosolids to produce py-oil and py-gas, as well as a valuable solid product, biochar, which can be used as a soil amendment or an adsorbent. If biosolids were pyrolized to produce biochar for use as an adsorbent,

WRRFs would be able to produce a valuable product while reducing overall biosolids that need to be managed. Previous fundamental research employing batch experiments has demonstrated that biosolids-derived biochar is a suitable sorbent for micropollutants (Tong, Mayer, and McNamara 2016; Yao et al. 2013). To move forward, research needs to be conducted to determine the feasibility of using biosolids-derived biochar as a sorbent to remove micropollutants from wastewater in a continuous flow-through column to better predict performance in on-site operations.

1.2 Objectives

The goal of this research was to determine the feasibility of using biosolids-derived biochar as a sorbent to remove triclosan, a representative micropollutant, from wastewater. Biosolids-derived biochar has been shown to remove organic micropollutants from water and wastewater solutions (Otero et al. 2003; Smith et al. 2009; Yu and Zhong 2006) and has potential to remove triclosan from wastewater effluent prior to being discharged to receiving waters. The specific objectives of this research were to determine the following in a continuous flow-through column with biosolids-derived biochar:

- Impact of pH on the removal of triclosan from water.
- Impact of flow rate on the removal of triclosan from water.
- Impact of organic micropollutant competition on the removal of triclosan from water.
- Impact of inorganic nutrients on the removal of triclosan from water.
- Feasibility of triclosan removal from secondary wastewater effluent.

- Performance of biosolids-derived biochar relative to commercial activated carbon and wood-derived biochar removal of triclosan.

1.3 Approach

Tong et al. (2016) revealed that biosolids-derived biochar could be used to adsorb triclosan by employing batch experiments. The current research project utilized column adsorption tests to determine the ability of biosolids-derived biochar to sorb triclosan from wastewater under continuous flow conditions. Triclosan is an antimicrobial compound and was selected for this research because it has been detected in surface waters and wastewater effluents and is often found in high abundance in biosolids. While triclosan will no longer be used in hand soaps due to being banned by the United States Food and Drug Administration (FDA), it is still used in the nation's top-selling toothpaste. Lab-scale column-sorption experiments were conducted to meet the objectives specified in Section 1.2. Experiments were conducted with triclosan-spiked Milli-Q water to individually adjust parameters such as nutrient content, and then experiments were conducted on actual wastewater. Triclosan was quantified using liquid chromatography mass spectrometry as described previously by Tong et al. (2016). Statistical software including Microsoft Excel and Graphpad Prism (Graphpad Software Inc., CA, USA) were used to determine triclosan removal efficiency during treatment.

1.4 Thesis Structure

The following chapters provide an in-depth description of this research into using biosolids-derived biochar as a sorbent for micropollutants. A review of the previous relevant literature is provided in Chapter 2. Experimental methods from this project are

presented in Chapter 3, and the results from experiments are presented in Chapter 4. Finally, Chapter 5 offers conclusions to summarize the work.

2 LITERATURE REVIEW

2.1 Importance of Micropollutants and Triclosan

Urbanization and anthropogenic activities have significantly contributed to the transport of a wide range of organic pollutants into receiving waters (Blair et al. 2013; Kolpin and Meyer 2002). The contamination of water supplies by organic chemicals has drawn much attention due to associated negative ecological and public health impacts (Reddy et al. 2014). More stringent environmental regulations have helped to mitigate the discharge of traditional contaminants into the environment including priority pollutants (compounds with known health effects such as herbicides, pesticides, and petroleum hydrocarbons), bacteria, nutrients, and heavy metals (Pal et al. 2014). However, there is growing concern related to the introduction of trace organic contaminants, or micropollutants as they will be referred to in this thesis, into the natural environment and the potential adverse impacts associated with exposure to these compounds, even at very low (µg/L or ng/L) concentrations (Inyang and Dickenson 2015; Gasperi et al. 2012).

Micropollutants are trace organic compounds found in many commercial products such as flame retardants, surfactants, plasticizers, industrial chemicals, and pharmaceuticals and personal care products (PPCPs) (Pal et al. 2014; Bernhardt et al. 2012). Micropollutants discharged to the environment can enter sewer conveyance systems where they are transported to WRRFs for treatment. Many micropollutants are recalcitrant to conventional wastewater treatment technologies and are discharged to the environment in liquid and solid effluents. This growing class of contaminants is generally comprised of compounds including hormones, antibiotics, endocrine disruptors,

pesticides and metabolites (Table 2.1) (Richardson, Exposure, and Agency 2003; Blair et al. 2013; Kolpin and Meyer 2002).

Table 2.1: Common representative micropollutants and their sources (Blair et al., 2013; Kolpin & Meyer, 2002).

Common Micropollutants	**Sources**
17β-estradiol (E2)	Natural estrogen
Bisphenol-A (BPA)	Plasticizer
Sulfamethoxazole (SMX)	Antibiotic medicine
Triclosan (TCS)	Antimicrobial, disinfectant

Triclosan [5-chloro-2-(2,4-dichlorophenoxy)-phenol] (TCS), is a commonly detected antimicrobial compound that is discharged to the environment from WWRFs in both the liquid effluent and residual biosolids (Heidler and Halden 2007; Lozano et al. 2013). TCS is found in a wide range of consumer products including hand soap, deodorant, lotion, surgical scrubs, and toothpaste (McMurry, Oethinger, and Levy 1998; Singer et al. 2002). TCS is a micropollutant of concern due to its prevalence in the natural environment and links to negative health effects in a wide variety of organisms (Blair et al. 2013; McNamara, Lapara, and Novak 2014). For example, TCS can impair swimming behavior in fathead minnows (Fritsch et al. 2013), cause toxicity in aquatic organisms (especially algae) (Orvos et al. 2002), and exposure to TCS has been linked to *Bacteria* with increased cross-resistance to other antimicrobial compounds (Daniel E. Carey and McNamara 2016; Carey et al. 2016). In engineered systems, elevated TCS concentrations can inhibit nitrification in activated sludge biomass, alter structure and function of anaerobic wastewater communities, and hinder methane production in

anaerobic digesters (Daniel E. Carey and McNamara 2015; McNamara, Lapara, and Novak 2014; Stasinakis et al. 2008). Triclosan is a synthetic organic chemical and its presence in WWRF effluents is an indicator that anthropogenic contaminants are not adequately removed through conventional treatment processes at WRRFs. Triclosan is being studied in this research as an indicator of how micropollutants can be removed via biosolids-derived biochar.

In September 2016, the United States Food and Drug Administration (FDA) announced that it would prohibit the sale of "consumer antiseptic washes" containing triclosan and 18 other antimicrobial compounds due to the inability of manufacturers to provide data on the safety and effectiveness of using these products (FDA 2016; McNamara and Levy 2016). This ban will prohibit the sale of consumer antiseptic washes containing these chemicals effective September 2017. However, this legislation will not address the numerous household personal care products, detergents, toothpastes, and industrial products that contain triclosan, and the worldwide usage of triclosan and related biocides is over a $7 billion/year industry (Heidler and Halden 2007; Zhou et al. 2013). It has been previously estimated that 4.2×10^5 kg of TCS are discharged from WWRFs annually (Heidler and Halden 2007) and TCS concentrations have been observed up to 133 mg/kg dry solids in U.S. biosolids and 2.7 µg/L in wastewater effluents (Bester 2003; McAvoy et al. 2002). Additionally, TCS is important to remove because it is recalcitrant in the natural environment with an estimated half-life of 104 days in soils amended with biosolids and around 540 days upon deposition in aquatic sediments (Lozano et al. 2012; Halden and Paull 2005).

Conventional wastewater treatment processes are not specifically designed for the removal of micropollutants such as TCS, and the removal of TCS from wastewater streams can vary substantially (Bester 2003; Heidler and Halden 2007). Additional studies have reported that PPCPs such as TCS, SMX, and metformin are present in detectable concentrations in Lake Michigan up to 3.2 kilometers away from the Milwaukee shoreline (Blair et al. 2013). Triclosan was detected in 58% of 139 U.S. streams surveyed with aqueous concentrations ranging from 0.14 to 2.3 µg/L (Kolpin and Meyer 2002). The presence of micropollutants in surface water systems poses ecological risks to aquatic species, as well as potential public health impacts associated with exposure to these compounds (Jung et al. 2013; Pal et al. 2014). Therefore, novel sustainable water treatment technologies capable of removing organic micropollutants from wastewater prior to being discharged to surface waters should be developed.

2.2 The Potential of Biochar for the Removal of Micropollutants from Wastewater

Several advanced tertiary treatment techniques have previously been investigated for the removal of micropollutants in WWRFs. Treatment processes such as membrane filtration, reverse osmosis (RO), UV treatment, and advanced oxidation methods have proven to be effective techniques for the removal of organic micropollutants, but are often associated with high infrastructure and operational costs (Kimura et al. 2003; Carballa et al. 2007; Manda, Worrell, and Patel 2014; Nghiem and Coleman 2008). Carbon based adsorbents such as activated carbon are commonly used in water treatment applications, and previous research has demonstrated the ability of a variety of carbonaceous sorbent materials for triclosan removal from aqueous solutions (Behera et al. 2010; Tong et al. 2016; Oh & Seo 2015). Activated carbon is commonly produced

from bituminous coal or coconut shells, and commercially available activated carbon can cost up to $1,500/ton (Ahmad et al. 2014). Replacing or augmenting traditional adsorbents such as activated carbon with biochar could greatly reduce treatment costs (e.g. $246/ton non-activated biochar) (Ahmad et al. 2012; Inyang and Dickenson 2015).

Biochar is a porous, carbon rich product that is produced via pyrolysis (thermochemical decomposition in the absence of oxygen) or the incomplete combustion of biomass, and has a high surface area to volume ratio (Ulrich et al. 2015; Oh and Seo 2015). Biochar has been growing in popularity in the last few decades as a potential soil amendment for agricultural gains and carbon sequestration, but also has demonstrated great potential as an adsorbent to remove pollutants from aqueous solutions (Mohan et al. 2014; Rajapaksha et al. 2016; Qian et al. 2015). Biochar can be produced from a variety of materials, including agricultural residue, animal litters, wood biomass, and sewage sludge or biosolids (Mohan et al. 2014; Xie et al. 2015; Tan et al. 2015). Biochar production from sewage sludge biosolids could provide a sustainable reduction in wastes produced from wastewater treatment processes such as activated sludge and also serve as an adsorbent to remove contaminants from water (Roberts et al. 2010; Oleszczuk et al. 2012; Smith et al. 2009; Hadi et al. 2015; Yu and Zhong 2006).

Recent research has demonstrated that thermochemical processes such as pyrolysis can potentially provide a biosolids handling process that offers simultaneous energy recovery and production of useful products such as biosolids-derived biochar (Agrafioti et al. 2013; Lu et al. 2013; McNamara et al. 2016). Pyrolysis of carbonaceous materials such as biosolids produces a solid phase charcoal-like product known as biochar, a liquid phase called py-oil, and a gas phase known as py-gas (Hoffman, Zitomer, and McNamara

2016; Ross et al. 2016). All three pyrolysis products are useful products, and could potentially help reduce biosolids disposal costs at WRRFs (McNamara et al. 2016). Additionally, the pyrolysis process itself removes micropollutants from biosolids (Hoffman, Zitomer, and McNamara 2016; Ross et al. 2016). Therefore, biochar that is used as an adsorbent for micropollutants could theoretically be re-pyrolyzed to remove the micropollutants from the biochar product.

2.3 Biochar as a Sorbent for Removal of Organic Micropollutants

Biochar has recently emerged as a potential replacement to activated carbon due to its low cost, relative abundance, and comparative sorptive abilities (Reddy et al. 2014; Inyang and Dickenson 2015; Kearns et al. 2014). Chemical modification/activation of biochars using acids, bases, and polymers can be beneficial for altering the surface chemistry and creating high-affinity sorption sites on the biochar surface for sorbing organic contaminants (Karakoyun et al. 2011; Tong, Mayer, and McNamara 2016; Rajapaksha et al. 2016; Nartey and Zhao 2016). Biochars from various feedstocks including wood debris, manure, and other agricultural wastes have demonstrated the ability to adsorb pollutants including volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), endocrine disrupting compounds (EDCs), and pesticides (Lefevre, Novak, and Hozalski 2012; Reddy et al. 2014; Jung, Oh, and Yoon 2015). For example, loblolly pine biochar adsorbents have successfully been used to remove pharmaceutical compounds from aqueous solutions including diclofenac, sulfamethoxazole, ibuprofen, and carbamazepine (Jung et al. 2013).

Similar to biochars from other feedstocks, biosolids-derived biochar has successfully been used to remove organic pollutants from wastewater and other aqueous

solutions (Otero et al. 2003; Smith et al. 2009). Recent research has demonstrated the ability of biosolids-derived biochar for TCS adsorption in batch equilibrium experiments, with observed adsorption capacities up to 872 μg/g (Tong, Mayer, and McNamara 2016). A similar study conducted with biosolids-derived biochar reported adsorption capacities up to 19.8 mg/g for fluoroquinolone antibiotics such as Gatifloxacin in batch-scale experiments (Yao et al. 2013). Yu and Zhong (2006) investigated the efficiency of various biosolids-derived sorbents for the removal of chemical oxygen demand (COD) and chromaticity color from wastewater streams through batch-scale adsorption tests and rapid small-scale column experiments. The results of the study demonstrated COD adsorption capacities up to 47.8 mg/g, and overall COD and chromaticity color removal rates of 79.1 and 87.5%, respectively (Yu and Zhong 2006).

Sorption of organic contaminants to biosolids-derived biochar has been attributed to various factors including its relatively high surface area, hydrophobicity, and interactions with oxygen-containing functional groups such as hydroxyl and carboxyl groups on the biochar surface (Hadi et al. 2015; Smith et al. 2009). Other studies have suggested that adsorption of organic compounds such as 4-chlorophenol to biosolids-derived biochar sorbents were influenced by dispersive interactions between the π-electrons of the solute aromatic ring and the adsorbent surface (Monsalvo, Mohedano, and Rodriguez 2011). Hydrogen bonding, hydrophobic interactions, and π-stacking may also contribute to the sorption of organic micropollutants such as triclosan from aqueous solutions (Lei, Hu, and He 2013; Tong, Mayer, and McNamara 2016).

Overall, recent research has established biosolids-derived biochar as a potential sorbent capable of the removal of organic pollutants from wastewater streams and

aqueous solutions. However, beyond batch sorption testing, there is limited information regarding the application of biosolids-derived biochar in adsorption/filtration systems for removing organic contaminants from drinking, potable reuse, or municipal waste waters. Column studies that have been performed with biochar have demonstrated the ability of biochar sorbents for the removal of EDCs such as BPA, atrazine, 17 α-ethinylestradiol (EE2), and estriol (E3) (Jung et al. 2013; Kumar, Mohan, and Sarma 2009). Additionally, previous studies have reported that Freundlich parameters based on column tests were different from those based on isotherm tests conducted via batch-scale experiments, and that adsorption parameters obtained from column tests could provide more realistic information for real world applications (Schindeman et al. 2012).

In the U.S., over 7 million tons of biosolids are produced annually, and approximately half of which are sent to landfills for disposal or incinerated (Zerzghi et al. 2010). The use of biosolids-derived biochar as a micropollutant sorbent advances sustainability initiatives by both encouraging biosolids reuse and enhancing micropollutant removal through wastewater treatment. Additional research in this area is necessary in order to gain a better understanding of the impact of various water qualities on the pollutant removal performance of biosolids-derived biochar.

2.5 Summary of Research Needs

Previous literature has suggested that organic micropollutants such as triclosan can be removed from wastewater via adsorption to biosolids-derived biochar. However, most studies have focused on batch equilibrium experiments, while the use of biosolids-derived biochar as a sorbent in a continuous flow-through column remains an understudied topic (Yu and Zhong 2006; Hadi et al. 2015). In this research, experiments

were conducted to determine if biosolids-derived biochar could remove triclosan from a variety of influent water and wastewater solutions. The effect of several parameters including pH, flow rate, organic micropollutant competition, and inorganic nutrient competition on triclosan removal from aqueous solutions were tested through column adsorption experiments.

The following hypotheses were tested corresponding to the five research objectives:

Objective 1: Determine the impact of pH on the removal of triclosan from water via biosolids-derived biochar in a continuous flow-through column.

Hypothesis: Based on triclosan having a pKa of 7.9, it was hypothesized that biosolids-derived biochar would remove more triclosan at lower bulk solution pH values.

Objective 2: Determine the impact of flow rate on the removal of triclosan from water via biosolids-derived biochar in a continuous flow-through column.

Hypothesis: Based on adsorption kinetics and previous literature regarding biochar adsorbents, it was hypothesized that biosolids-derived biochar will remove more triclosan at lower flow rates.

Objective 3: Determine the impact of organic micropollutant competition on the removal of triclosan from water via biosolids-derived biochar in a continuous flow-through column.

Hypothesis: Triclosan removal via biosolids-derived biochar will be decreased in the presence of other organic micropollutants due to competition for adsorption sites on the biochar surface.

Objective 4: Determine the effect of inorganic nutrient competition on the removal of triclosan from water via biosolids-derived biochar in a continuous flow-through column.

Hypothesis: Triclosan removal via biosolids-derived biochar will be decreased in the presence of inorganic nutrients, phosphate and ammonium, due to competition for adsorption sites on the biochar surface.

Objective 5: Determine the feasibility of triclosan removal from secondary wastewater effluent via biosolids-derived biochar in a continuous flow-through column.

Hypothesis: Biosolids-derived biochar will remove triclosan from secondary wastewater effluent, but not as efficiently as previous tests with Milli-Q water.

Objective 6: Compare triclosan removal performance of biosolids-derived biochar relative to commercial activated carbon and commercial biochar in a continuous flow-through column.

Hypothesis: Triclosan removal via biosolids-derived biochar will be less than commercial activated carbon, but will be superior to commercial biochar.

3 METHODOLOGY

3.1 Adsorbents

The feedstock for the biosolids-derived biochar in this study was Milorganite®, a heat-dried blend of waste activated sludge and anaerobically digested primary solids, which is produced by the Milwaukee Metropolitan Sewerage District (MMSD) in Milwaukee, WI. The feedstock was pyrolized to produce biochar by placing 30-50 g of Milorganite® into a 250-mL flask, purging with argon gas for 15 minutes, capping with aluminum foil, and heating in a muffle furnace for 60 minutes at 600°C. The biochar was cooled in a desiccator to room temperature prior to conditioning for adsorption tests.

All biosolids-derived biochar was washed with Milli-Q® (Billerica, MA) water to remove residual surface impurities and ash prior to acid washing. The acid conditioning consisted of mixing 1 N HCl with the biochar in a 1 L flask at a dosage of 1 g biochar per 10 mL HCl. The mixtures were sealed and agitated on a shaker table at 150 rpm for 24 hours. The biochar slurry was filtered with Whatman® (Ann Arbor, MI) 0.7 µm glass fiber filters via vacuum filtration. The recovered biochar was rinsed three or more times with Milli-Q water to remove ash and remaining acid prior to being dried in a 103°C oven and stored in a desiccator prior to use in adsorption experiments.

Adsorption experiments were also conducted with one pine wood-based biochar produced by Biochar Now in Berthoud, CO (BN-biochar) and one activated carbon produced by Calgon Carbon, Pittsburgh, PA (Calgon Filtrasorb® 300) (CF300-AC). The wood-based biochar and coal-based activated carbon were used to compare triclosan adsorption with that of the biosolids-derived biochar. The BN-biochar was subjected to

the same acid washing protocol as the BS-biochar. The CF300-AC was not modified prior to use in column adsorption experiments, but was activated through steam activation processes by the manufacturer.

3.2 Column Adsorption Experiments

Column adsorption tests were conducted to determine the removal of triclosan from water and wastewater solutions via biosolids-derived biochar under continuous flow conditions. Experiments were conducted to determine the impacts of various parameters of wastewater on triclosan removal. The parameters tested in this study included bulk solution pH, flow rate, organic micropollutant competition, and inorganic nutrient competition. Adsorption tests were also conducted with secondary wastewater effluent obtained from the Jones Island Water Reclamation Facility, Milwaukee, WI.

All glassware used was silanized using 5% by volume dichlorodimethylsilane (99.5%, Sigma Aldrich, St. Louis., MO, USA) and 95% by volume heptane (99%, Sigma Aldrich, St. Louis, MO, USA) solution to prevent chemicals from adsorbing onto the glass surface. Triclosan (97%, Sigma Aldrich, St. Louis, MO, USA) was pre-dissolved in HPLC-grade methanol (99%, Sigma Aldrich, St. Louis, MO, USA) and stored at 4°C for use as stock solution. The volumetric ratio of methanol/TCS stock to water was less than 0.5% for all adsorption tests, which reduces co-solvent effects (Schwarzenbach, Gschwend, and Imboden 2003; Tong, Mayer, and McNamara 2016).

Fixed-bed column experiments were conducted using 11 mm inner diameter and 60 cm length glass columns (Ace Glass Incorporated, Vineland, NJ, USA). The glass columns were packed with biochar or activated carbon adsorbents (bed depth 5-10 inches) between two supporting layers of glass wool and glass beads. The adsorption

columns were operated at room temperature and fed via a peristaltic pump (Syringe Pump NE-9000G, New Era Pump Systems Inc., Farmingdale, NY, USA) programmed at a constant volumetric flow rate. Column influent and effluent samples were collected at different time intervals and analyzed for the target constituents (e.g. triclosan). The experimental setup used for the column adsorption experiments is shown in Figure 3.1.

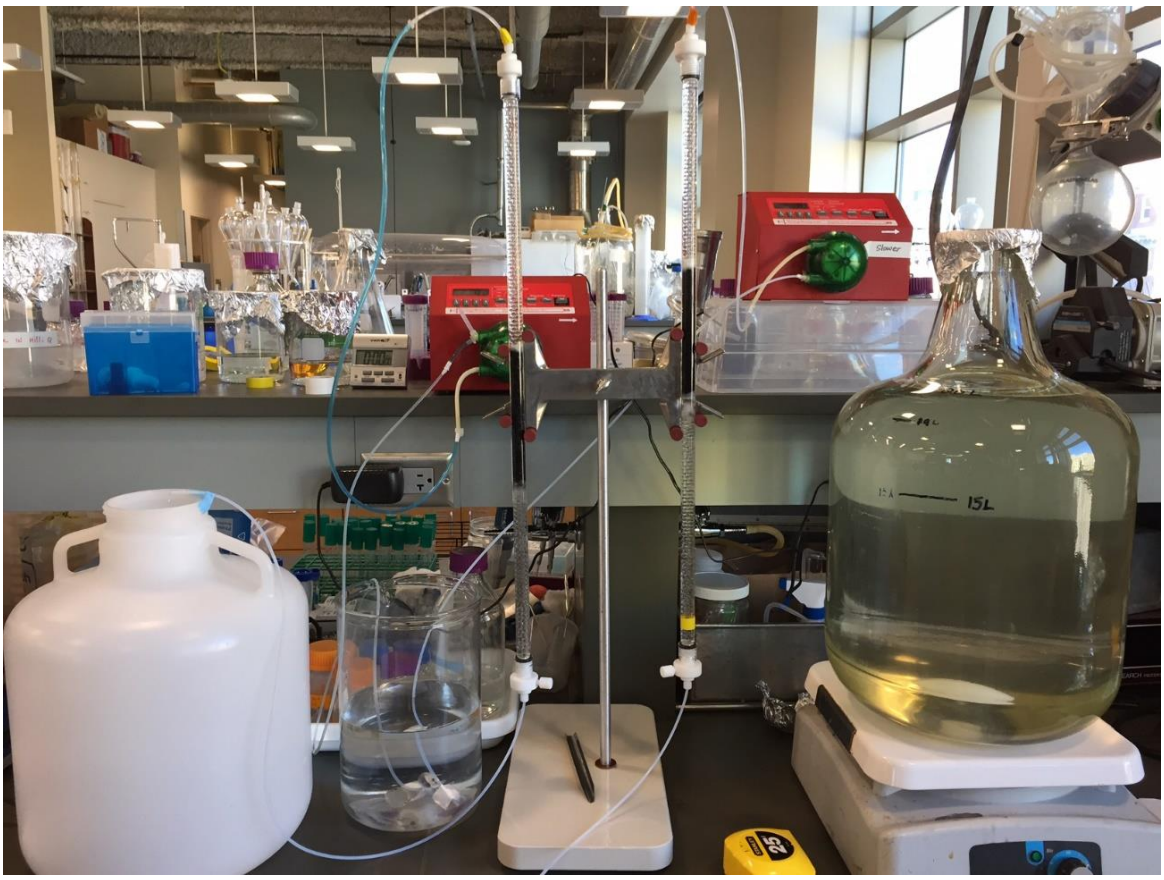

Figure 3.1. Column adsorption experimental setup. Influent 20 L vessel is shown on the right, and was used to simultaneously feed two glass columns packed with adsorbents. Peristaltic pumps were used to pump feed water into the columns, and samples were collected from effluent tubes prior to entering effluent vessel (shown on left).

3.2.1 Impact of Bulk Solution pH on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of bulk solution pH on the triclosan adsorption to biosolids-derived biochar in continuous flow-through columns. Neutral pH values were investigated for practical water treatment applications. The influent water pH was adjusted to 7 or 8.5 using 0.1 N HCl or NaOH. Triclosan was added at a concentration of approximately 150-250 µg/L for all pH experiments. Influent and effluent water samples were collected from the column test and analyzed for TCS. Triplicate column experiments were conducted for each pH tested to assess variation among replicates.

3.2.2 Impact of Flow Rate on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of flow rate on triclosan adsorption to biosolids-derived biochar in continuous flow-through columns. Volumetric flow rates were controlled using a peristaltic pump, and ranged from 10 to 40 mL/min, which is equivalent to a hydraulic loading rate (HLR) of 2.6 and 10.3 gpm/ft^2, respectively. The flow rate adsorption experiments were conducted at pH 7, and TCS was added at a concentration of approximately 250-500 µg/L for flow rate experiments. Higher influent TCS concentrations were used for flow rate experiments to reduce the time to reach TCS breakthrough in column effluent. Influent and effluent water samples were collected from the column test and analyzed for TCS.

3.2.3 Impact of Organic Micropollutants on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of multiple organic micropollutants on triclosan adsorption to biosolids-derived biochar in a continuous flow-through column. The competitive adsorption experiments consisted of

the addition of three micropollutants into Milli-Q water adjusted to pH 7. The representative organic micropollutants used in this study included E2, TCS, and SMX. The same methods as single solute experiments were used for TCS stock solution preparation. E2 (98%, Sigma Aldrich, St. Louis, MO, USA) and SMX (Sigma Aldrich, St. Louis, MO, USA) were pre-dissolved in HPLC-grade methanol (99%, Sigma Aldrich, St. Louis, MO, USA) and stored at 4°C for use as stock solutions. The organic micropollutants were individually added at a concentration of approximately 350 µg/L for the micropollutant competition experiments. Influent and effluent water samples were collected from the column test and analyzed for E2, TCS, and SMX.

3.2.4 Impact of Inorganic Nutrients on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of inorganic nutrients on triclosan adsorption to biosolids-derived biochar in a continuous flow-through column. Nutrients such as phosphate and ammonia are present in wastewater streams, at much higher concentrations than micropollutants, and these ionic species could potentially compete for adsorption sites on the biochar surface. The competition experiments consisted of the addition of ammonium (NH_4^+) as ammonium chloride, NH_4Cl (99.8%, Fisher Scientific, Pittsburgh, PA, USA) and phosphate (PO_4^{3-}) as potassium phosphate dibasic anhydrous, K_2HPO_4 (99.2%, Fisher Scientific, Pittsburgh, PA, USA).

Inorganic nutrients were added to Milli-Q water solutions containing TCS at concentrations of approximately 1 mg/L as PO_4-P and 50 mg/L as NH_4-N for the competition experiments by adding 0.5625 g K_2HPO_4 and 3.44 g NH_4Cl into a 20 L solution with Milli-Q water. These concentrations of nutrients were chosen to evaluate

TCS removal simulating a range of conditions, such as anaerobic membrane bioreactor effluent that would contain micropollutants and nutrients. TCS was added at a concentration of approximately 350 µg/L for the inorganic competition experiments.

3.2.5 Impact of Secondary Wastewater Matrix on Triclosan Removal

Column adsorption experiments were conducted to determine the overall removal of triclosan from secondary wastewater effluent via biosolids-derived biochar in a continuous flow-through column. Municipal secondary-treated wastewater effluent samples were obtained from Jones Island Water Reclamation Facility, Milwaukee, WI, and were used to investigate triclosan adsorption to biosolids derived-biochar in complex matrices. Wastewater adsorption experiments were also conducted with pine wood-derived biochar and activated carbon to compare the removal of triclosan using a variety of carbonaceous adsorbents. Water quality parameters including pH, conductivity, COD, total organic carbon (TOC), NH_3-N, PO_4-P, and solids were quantified.

Parameters such as pH and conductivity were measured over the course of the adsorption experiments at time (T) T= 0, 60, 300, 1440, and 2880 minutes of operation. COD, TOC, NH_3-N, PO_4-P, and solids fractions including Total Solids (TS), Total Volatile Solids (VS), Total Fixed Solids (FS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Fixed Suspended Solids (FSS), Total Dissolved Solids (TDS), Volatile Dissolved Solids (VDS), and Fixed Dissolved Solids (FDS) were measured for secondary wastewater effluent characterization. TCS stock solution was added to wastewater effluent at approximately 500 ug/L. To investigate adhesion of TCS to wastewater solids, an adsorption column without biochar was used as a control. The

background TCS concentration in the secondary wastewater effluent was below detection limit (2 µg/L).

3.3 Sample Processing and Characterization

3.3.1 Micropollutant Analysis

At each sampling time, approximately 4 mL of column effluent was collected into a glass amber vial for subsequent micropollutant analysis. Water samples were stored at 4°C for 1-2 days prior to being mixed with HPLC grade methanol (50:50) and filtered through 0.45 µm PTFE filters into 2 mL amber LC-MS vials. Aqueous phase E2, TCS, and SMX were measured with liquid chromatography-mass spectrometry (LC-MS/MS) (LCMS-2020, Shimadzu Corporation, MD, USA). LC-MS/MS methodology previously described by (Ross et al. 2016; Tong, Mayer, and McNamara 2016) was modified as described in the next paragraph and applied for quantification of target analytes.

A binary gradient of Milli-Q water and 100% HPLC-grade methanol was used as the eluent. The gradient began at 80% methanol, raised to 100% methanol at 8 minutes, ramped down to 80% methanol from 8 to 9 minutes and remained at 80% methanol to 13 minutes to allow column re-equilibration. The eluent flow rate was 0.4 mL/min. Sample injections of 20 µL were passed through a Phenomenex® (Torrance, CA, USA) Luna 3u C18 reverse-phase column (150×3 mm, 100 Å pore size). TCS was detected via mass-spectrometry with negative electrospray ionization (ESI-), at a mass-to-charge (*m/z*) ratio of 287. The (*m/z*) ratio is 271 for E2 and 252 for SMX.

Identification of target analytes was based on the presence of parent compounds eluting from the column at the same retention time as standards. Quantification is based on the linear regression analysis of sample peak area to that of at least a 5-point standard

curve developed for each compound. Quantification limits for TCS, E2, and SMX using a signal-to-noise ratio of 10:1 were 2, 7, and 10 µg/L, respectively.

Recovery of TCS from secondary wastewater effluent was verified through the addition of an internal standard prior to LC-MS/MS analysis. The internal standard used in this study was TCS ($^{13}C_{12}$, 99%) (Cambridge Isotope Laboratories, Inc., Andover, MA, USA). A known amount (0.4 µL) of TCS internal standard was added to every sample, standard, and blank prior to analysis. A calibration curve was constructed for known concentrations of internal standard versus the ratio of target analyte (TCS) response to the internal standard response for each sample. The complex nature of high matrix samples almost eliminates the possibility of 100% recovery of target analytes from their respective sample matrices, in this case wastewater effluent. However, due to the internal standard calibration, the reproducibility of the ratio of TCS to the internal standard in processed samples was increased, as well as method precision.

3.3.2 Water Sampling and Characterization

Secondary effluent wastewater samples were collected from Jones Island Reclamation Facility, Milwaukee, WI. Wastewater was collected in 10 or 20 L plastic carboys, and was stored at 4°C until use in adsorption experiments within 2 days of collection. Water quality parameters that were analyzed immediately upon collection included pH, COD, and solids fractions. Wastewater samples for phosphate and ammonium were preserved with sulfuric acid (36 N) to pH below 2 and stored at 4°C until analysis. TOC samples were collected in 40 mL glass cuvettes and were stored at 4°C until analysis. Appropriate Standard Methods used for wastewater characterization and analysis are included in Table 3.3.

Table 3.3: Standard Methods used for secondary wastewater effluent characterization (APHA et al., 1998).

Parameter(s)	Standard Method(s)	Method Number(s)
Phosphate	Ascorbic Acid Method	4500-P-E
Ammonia	Phenate Method	4500-NH_3-F
TS, VS, FS	Total Solids	2540-B, 2540-E
TSS, VSS, FSS	Total Suspended Solids	2540-D
TDS, VDS, FDS	Total Dissolved Solids	2540-C
COD	Chemical Oxygen Demand	5220-D

3.4 Characterization of Adsorbents

3.4.1 Surface Area Analysis

Biochar and activated carbon specific surface areas were measured via N_2 gas sorption at 77 K using a Brunauer-Emmett-Teller (BET) automated surface analysis instrument, Autosorb iQ2 (Quantachrome Instruments, Boynton Beach, FL, USA). MultiPoint BET surface area analysis results are reported in m^2/g of adsorbent. The average pore radius was determined and is reported in units of Angstroms (Å). Total pore volume for pores with radius less than 2.82 Å at P/Po = 0.000067 was determined for each adsorbent, in addition to the total micropore volume as determined by the t-method (Shimabuku et al. 2016; Rozada et al. 2005; Zhu et al. 2014). Pore volume data for adsorbents is reported in cm^3/g of adsorbent.

3.4.2 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) was used to analyze surface functional groups on the adsorbent surfaces. A Shimadzu IR Tracer 100 (Shimadzu Corporation, MD, USA) was used to investigate biochar and activated carbon surface

functional groups. FTIR spectral analyses can be used to help elucidate the role of functional groups on adsorption of molecules from aqueous solutions (Hadi et al. 2015; Ahmad et al. 2014). FTIR spectra were recorded from 4,000 to 150 cm^{-1} and plotted versus percent transmittance.

3.4.3 SEM Imaging

Scanning electron microscopy (SEM) was used to compare surface morphology of the adsorbents. Granular biochar and activated carbon were dried and adhered to a SEM specimen mount with carbon tape. The surface morphology was observed via JEOL JSM-6510LV SEM (JEOL USA, Inc., MA, USA) at an accelerating voltage of 15 kV and magnifications ranging from x20 to x1000.

3.5 Analyses

Column adsorption experiments were compared to evaluate TCS removal from water and wastewater solutions. Experiments were compared by the number of bed volumes treated before mass breakthrough of TCS was observed in the column effluent. Mass breakthrough was defined as the number of bed volumes treated corresponding to when 5% of the influent TCS mass was detected in the effluent (Schindeman et al. 2012; Schwarzenbach, Gschwend, and Imboden 2003; ASTM 2013). The mass of TCS removed after 2,000 bed volumes treated through each column was also quantified and used to compare the adsorption experiments. This number of bed volumes was chosen for comparison due to observed decreases in performance of columns after this time (reduced flow rates due to clogging) during laboratory wastewater adsorption experiments. Additionally, previous studies have reported that exhaustion of GAC filters for trace organic contaminants is substantially longer than for natural organic matter

(NOM), and that methods appropriate for estimating GAC replacement frequency for NOM removal are not directly applicable in regards to trace organic contaminant removal (Schindeman et al. 2012). Similarly, several studies have reported that quantitative results obtained from rapid small scale column tests (RSSCTs) and pilot-scale studies for trace organic contaminants can significantly overestimate GAC service life (Crittenden et al. 1991; Knappe et al. 1997).

Other column parameters determined for each column adsorption experiment included empty bed contact time (EBCT) and carbon usage rate (CUR). EBCT is a measure of the time during which a water stream being treated is in contact with the treatment medium (e.g. BS-biochar) in the contact vessel, assuming that all liquid passes through at the same velocity. EBCT was calculated by dividing the volume of the empty bed by the flow rate. CUR was determined for each column adsorption experiment by dividing the grams of TCS removed by the total volume (mL) of solution treated. CUR is the reciprocal of specific throughput, and relates the volume of influent solution treated to the mass of adsorbent used.

GraphPad Prism 7.02 was used for statistical analysis including non-linear analysis of breakthrough curves. Non-linear regression of column adsorption data was fit using saturation function models to obtain best-fit values of C_e/C_o max and Kc. Reported values for C_e/C_o max represent the maximum C_e/C_o value for TCS observed during each column adsorption experiment. Reported Kc values indicate the number of bed volumes passed through the column corresponding to C_e/C_o values equal to half of the observed C_e/C_o max. Saturation function models were used due to having the best fit for column adsorption data, and the model assumptions were similar to Langmuir adsorption

isotherms, which assumes that a limited number of adsorption sites exists on an adsorbent surface and that each site can hold at most one molecule of adsorbate. R^2 values are reported for each adsorption experiment fit with non-linear regression.

4 RESULTS & DISCUSSION

4.1 Impact of Bulk Solution pH on Triclosan Removal

The bulk solution pH was the first variable tested on column experiments to determine if fluctuations around typical effluent pH values would impact sorption. Evaluating the relationship between pH and triclosan adsorption is critical from a practical water treatment standpoint, as well as a mechanistic perspective, because it helps to understand which mechanisms of adsorption play major roles in removal. Triclosan has a pKa of 7.90, so pH values below (pH 7) and above (pH 8.5) were selected for testing to explore the influence of charge on removal.

The adsorption of triclosan to BS-biochar was not significantly different between column experiments conducted at pH 7 and 8.5 (p value = 0.08), as shown in Figure 4.1. These results are congruent with previous research using BS-biochar as an adsorbent, which reported no statistical difference in sorption capacity of BS-biochar for TCS in batch equilibrium experiments conducted from pH 5 to 9 (Tong, Mayer, and McNamara 2016).

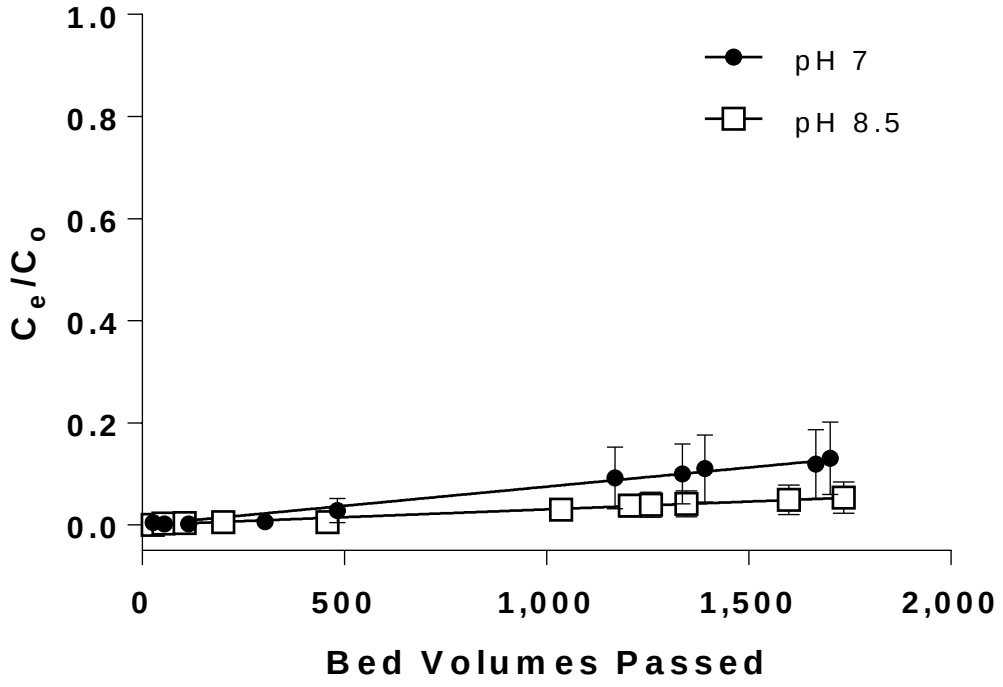

Figure 4.1. Impact of bulk solution pH on triclosan removal. Experiments were conducted at pH 7 and 8.5. All experiments had a flow rate of 10 mL/min and 10 g of BS-biochar adsorbent were packed into glass columns. TCS was added to Milli-Q water solutions of approximately 150-250 µg/L for pH experiments. C_e is defined as the effluent concentration and C_o is the average influent concentration. Error bars represent ± 1 standard deviation of triplicate experiments.

The number bed volumes passed prior to observing mass breakthrough of TCS, defined as when 5% of the influent TCS mass was detected in the effluent, for pH 7 experiments ranged from 998 to 1,495. Mass breakthrough of TCS for pH 8.5 tests was only observed in one adsorption experiment and occurred after 1,615 bed volumes. The observed CURs (reciprocal of specific throughput), which relate the volume of influent solution treated to the mass of adsorbent used in the column, were 5.03×10^{-4} g TCS/mL treated on average for pH 7 experiments, compared to 5.17×10^{-4} g TCS/mL for pH 8.5 tests. The observed CURs for pH 7 and 8.5 experiments were not significantly different

(p value = 0.51). EBCT for all the pH adsorption experiments was calculated to be 2.0 minutes. Non-linear analysis of breakthrough curves was performed using GraphPad Prism, however, poor fit was observed due to the adsorption experiments not approaching saturation of the adsorbent. Observed R^2 values for pH 7 and 8.5 experiments were 0.64 and 0.60, respectively.

Most water/wastewater treatment applications are employed at near-neutral pH values from 6.5 to 8.5, and a similar pH range was tested in this study since BS-biochar would most likely be used in near neutral pH solutions for wastewater treatment applications. Additionally, the dissociation constant (pKa) of triclosan is 7.90, and when the bulk influent solution has a pH of 7, neutral TCS molecules will be the dominant species in solution (approx. 75%). The neutral form of TCS is more hydrophobic than the ionized form, and previous research has suggested that the adsorption of TCS from aqueous solutions increases with lower bulk solution pH (Tong, Mayer, and McNamara 2016; Zhou et al. 2013). Notably, others found TCS adsorption increased at a bulk influent solution pH of 3, but no statistical difference in TCS adsorption to BS-biochar was observed from experiments conducted from pH 5 to 9 (Tong, Mayer, and McNamara 2016). These studies concluded that direct electrostatic attraction is unlikely to contribute to TCS sorption to BS-biochar, and that hydrogen bonding may play a more prominent role as TCS has both hydrogen donor and acceptor moieties. It was hypothesized in this study that TCS removal would be increased at lower bulk solution pH. However, the results did not support this hypothesis, presumably due to stronger hydrophobic interactions compared to electrostatic forces between TCS molecules and the BS-biochar surface.

Tong et al. (2016) determined that the point of zero charge (PZC) of HCl-treated BS-biochar produced at 600°C was approximately 3.28-3.50. There is an overall net negative surface charge of the biochar when the solution pH is greater than the PZC, thus repulsing anions. Although a hydroxyl functional group is present, TCS is still a relatively hydrophobic compound with a log K_{ow} of 4.76 and remains highly hydrophobic in nature even in ionized form (Behera, Oh, and Park 2010). The relatively high octanol-water partitioning coefficient of TCS suggests that adsorption of TCS from aqueous solutions may be influenced most by hydrophobic interactions, π-π bonds, and hydrogen bond formation (Lei, Hu, and He 2013; Tong, Mayer, and McNamara 2016). The results from previous studies involving TCS adsorption are consistent with the results of the current study as there was no significant difference between triclosan removal from aqueous solutions conducted at pH 7 and 8.5. For practical applications, subsequent TCS adsorption experiments were conducted at pH 7, since wastewater effluent pH is unlikely to be adjusted to achieve higher micropollutant removal.

TCS adsorption experiments were conducted in triplicate to determine reproducibility and variation among identical column adsorption experiments. Breakthrough curves for each treatment group demonstrated high reproducibility and demonstrated similar trends in TCS removal for the duration of the column studies. The mass of TCS removed after 1,000 bed volumes treated in pH 7 adsorption experiments was determined to be 130, 170, and 180 µg/g BS-biochar for the three replicates (Mean/SD = 160 µg/g ± 26). TCS adsorption at a pH of 8.5 removed 180, 230, and 260 µg/g BS-biochar for triplicate experiments (Mean/SD = 220 µg/g ± 40). However, not all adsorption experiments were conducted at the exact same initial concentration (ranged

from 150 to 250 µg/L), which likely contributed to variation in TCS mass removed after 1,000 bed volumes among treatment groups. Additionally, the heterogeneity of the feedstock (municipal wastewater biosolids) could have contributed to the variation among replicates.

4.2 Impact of Flow Rate on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of flow rate on triclosan adsorption to BS-biochar in continuous flow-through columns. Volumetric flow rates were controlled using a peristaltic pump, and ranged from 10 to 40 mL/min, which is equivalent to a surface loading rate (SLR) of 2.6 to 10.3 gpm/ft^2, respectively. SLRs for granular activated carbon (GAC) filters at drinking water treatment plants typically range between 2 to 10 gpm/ft^2 (EPA 2017). As flow rate increased, TCS adsorption to BS-biochar decreased (Figure 4.2).

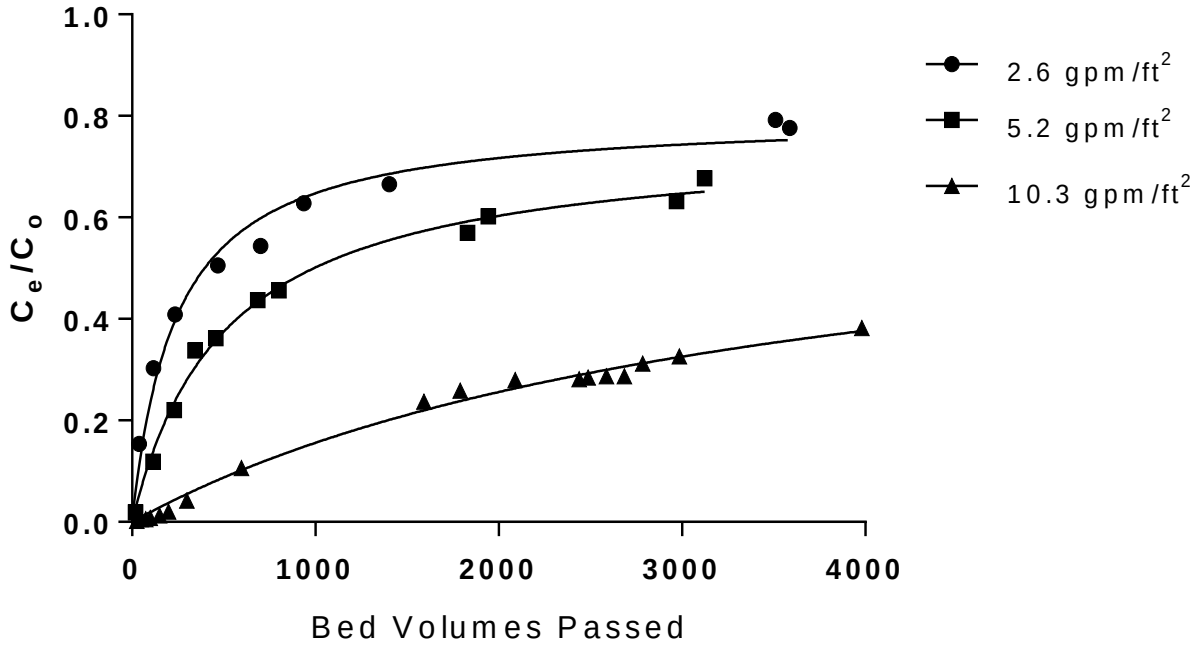

Figure 4.2. Impact of flow rate on TCS removal. Experiments were conducted at pH 7, 5 grams of biosolids-derived biochar adsorbent, and TCS was added to Milli-Q water solutions of approximately 500 µg/L for flow rate experiments.

The number of bed volumes passed prior to observing mass breakthrough of TCS in column effluent for the 2.6 gpm/ft^2 flow rate test was 1,371, while mass breakthrough was observed after 1,013 and 450 bed volumes for 5.2 gpm/ft^2 and 10.3 gpm/ft^2 flow rates, respectively. Corresponding EBCT values for the flow rate experiments were 0.25 minutes (10.3 gpm/ft^2), 0.5 minutes (5.2 gpm/ft^2), and 1.0 minutes (2.6 gpm/ft^2). Observed CURs were determined to be 1.1 x 10^{-3} g TCS/mL treated for 10.3 gpm/ft^2, 3.1 x 10^{-4} g TCS/mL for 5.2 gpm/ft^2, and 2.3 x 10^{-4} g TCS/mL for 2.6 gpm/ft^2. The mass of TCS removed by adsorption to BS-biochar after 2,000 bed volumes passed was 700 µg/g for 10.3 gpm/ft^2, compared to 896 µg/g and 1.53 mg/g for 5.2 gpm/ft^2 and 2.6 gpm/ft^2 tests, respectively. The highest removal rate and adsorption capacity was observed for

slower flow rates, which was attributed to increased contact time for adsorbate (TCS) molecules to sorb onto the BS-biochar surface.

Non-linear analysis was performed for the flow rate experiments to obtain C_e/C_o max and Kc values for each different flow rate tested. Calculated C_e/C_o max values for flow rate experiments were 0.80 (R^2= 0.97) for 10.3 gpm/ft^2, 0.76 (R^2= 0.99) for 5.2 gpm/ft^2, and 0.72 (R^2= 0.99) for 2.6 gpm/ft^2 flow rate experiments. C_e/C_o max values indicate the maximum value for C_e/C_o observed for each experiment, and observed C_e/C_o max values increased with higher flow rates, which indicates decreased removal performance. Corresponding Kc values (bed volumes to half C_e/C_o max) were 240 bed volumes for 10.3 gpm/ft^2, 519 bed volumes for 5.2 gpm/ft^2, and 3,583 bed volumes for 2.6 gpm/ft^2 experiments. The reduction in Kc values with increasing flow rate indicates a shorter time to reach mass breakthrough of TCS in column effluent. Overall, the results of the flow rate experiments indicate increased TCS removal using BS-biochar at slower flow rates, and significantly more bed volumes treated prior to decreased removal performance.

The reduction in TCS removal for higher flow rates was presumably due to a shorter EBCT, which reduced the contact time between the TCS molecules and biochar surface. Increased contact time between adsorbent and adsorbate molecules allows for the adsorption of more TCS and thus an improved shape (e.g. slower rise) in the breakthrough curve. This reduction in mass breakthrough reduces the CUR (less BS-biochar mass per volume treated), and would allow for longer filter runs with higher removal efficiency. Additionally, the EBCT is a crucial design parameter when sizing carbon filters for WWRF effluent treatment, and longer EBCTs typically lead to

improved retention of adsorbates and higher removal efficiency (Crittenden et al. 1991; Schindeman et al. 2012; Zietzschmann et al. 2014). However, maximizing EBCT for increased contaminant adsorption means increasing the size of filter beds and/or retention time, which can be limited in flexibility in operations where specific volumetric flows must be treated. As a result, an appropriate balance between EBCT and desired removal efficiency must be determined for contaminants of interest in a particular application.

4.3 Impact of Organic Micropollutants on Triclosan Removal

Column adsorption experiments were conducted to determine the impact of multiple organic micropollutants on triclosan adsorption to biosolids-derived biochar in a continuous flow-through column. For the competitive adsorption experiments, E2 and SMX were added as representative micropollutants due to their prevalence in the natural environment and frequent detection in liquid effluent from WRRFs (Blair et al. 2013; Lozano et al. 2013; Heidler and Halden 2007).

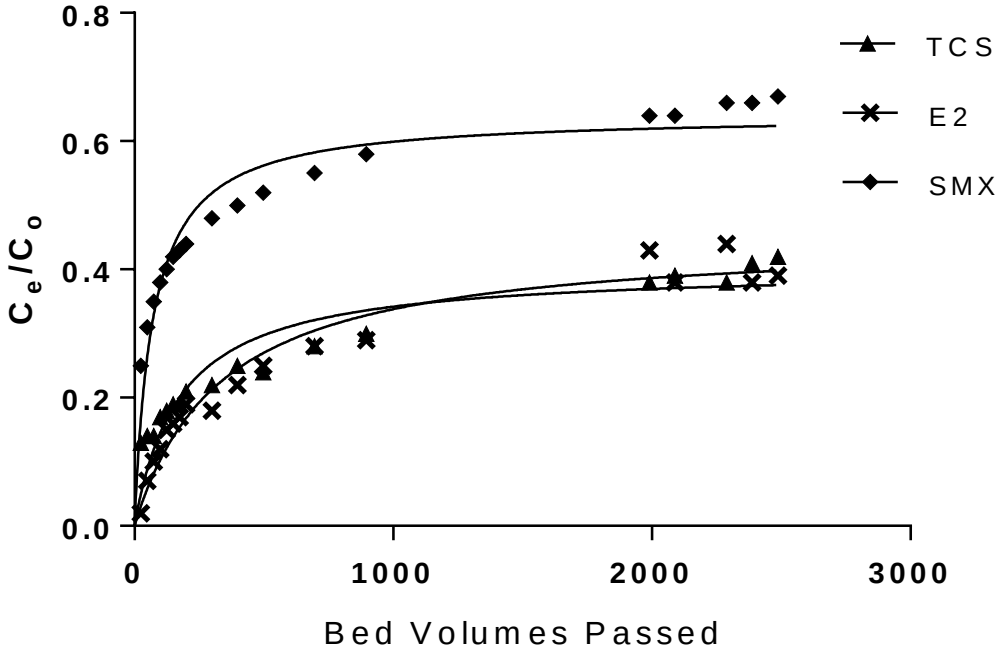

Figure 4.3. Impact of organic micropollutant competition on triclosan removal. Experiments were conducted at pH 7, 10 mL/min flow rate, 6 grams of biosolids-derived biochar adsorbent. Micropollutants (E2, TCS, SMX) were added to Milli-Q water at approximately 350 µg/L each for micropollutant competition experiments.

Note: For clarity, maximum value shown on y-axis for C_e/C_o is 0.8, rather than 1.0 as shown in previous figures.

The addition of organic micropollutants decreased TCS removal compared to previous single solute adsorption experiments, but BS-biochar demonstrated capability to remove all three micropollutants (Figure 4.3). Mass breakthrough of TCS occurred after 675 bed volumes passed with the competition of E2 and SMX in solution, compared to 780 bed volumes for single solute experiments with only TCS. The calculated EBCT value for the micropollutant competition experiment was 1.2 minutes, and CUR was determined to be 3.2×10^{-4} g TCS/mL treated. The mass of TCS removed at 2,000 bed volumes treated was 517 µg/g of TCS, however, the BS-biochar also removed 500 µg/g

of E2 and 300 µg/g of SMX. Total MP removal after 2,000 bed volumes treated was 1.32 mg/g BS-biochar.

The results of the current study demonstrate that BS-biochar can simultaneously sorb multiple organic micropollutants from aqueous solutions. Matrices such as secondary wastewater effluent would contain many trace organic compounds, albeit and much lower individual concentrations, and it is important to study the effects of multiple organic constituents on the performance of BS-biochar as an adsorbent. Additionally, the micropollutants selected in this study have various chemical and physical characteristics and help to demonstrate the efficiency of BS-biochar for the removal of a variety of pollutants. It is also important to note that micropollutant additions were much higher than environmentally relevant concentrations in the current study, but were chosen at these concentrations to allow for better quantification of percent removal through column adsorption tests.

Observed breakthrough curves for micropollutants suggest that BS-biochar has an increased affinity for more hydrophobic compounds such as E2 and TCS, compared to more hydrophilic compounds such as SMX. Observed C_e/C_o max values for the adsorption of micropollutants to BS-biochar were determined to be 0.40 (R^2= 0.87) for TCS, 0.45 (R^2= 0.96) for E2, and 0.64 (R^2= 0.92) for SMX. The corresponding log K_{ow} values for the micropollutants tested are 4.01 for E2 and 4.76 for TCS, compared to 0.89 for SMX. The smaller log K_{ow} of SMX indicates the tendency of the compound to remain in the aqueous phase, which is demonstrated by the decreased removal of SMX compared to E2 and TCS. Additionally, the pKa of SMX is 5.79, which indicates that a larger fraction of SMX molecules would be negatively charged in solution at neutral pH

ranges. Similar batch-scale adsorption studies have reported inferior adsorption of SMX to biochar compared to more hydrophobic compounds, which was attributed to its low hydrophobicity and π-energy (Jung et al. 2013). Moreover, organic contaminants such as SMX are anionic in solution at neutral pH values, and reduced affinity for adsorption to BS-biochar may also be influenced by the net negative surface charge of BS-biochar (thus repulsing anions) (Shimabuku et al. 2016; Tong, Mayer, and McNamara 2016; Thompson et al. 2016). However, the ability of BS-biochar to remove both hydrophobic and hydrophilic organic contaminants is evident from the results of the current study, and has been previously attributed to adsorption mechanisms such as hydrogen bonding and π- π interactions between aromatic rings on the adsorbent surface and adsorbate π-electrons (Lei, Hu, and He 2013; Monsalvo, Mohedano, and Rodriguez 2011).

4.4 Impact of Inorganic Nutrients on Triclosan Removal

The impact of inorganic nutrient competition on triclosan adsorption to BS-biochar in continuous flow-through columns was investigated. Nutrients such as phosphate and ammonium are present in wastewater streams and these ionic species could potentially compete for adsorption sites on the biochar surface. Mass breakthrough of TCS in column effluent was significantly reduced in the presence of inorganic nutrients (indicating competition between nutrients and TCS for adsorption sites) and was observed after 450 bed volumes passed compared to 780 bed volumes when nutrients were not present in solution (Figure 4.4).

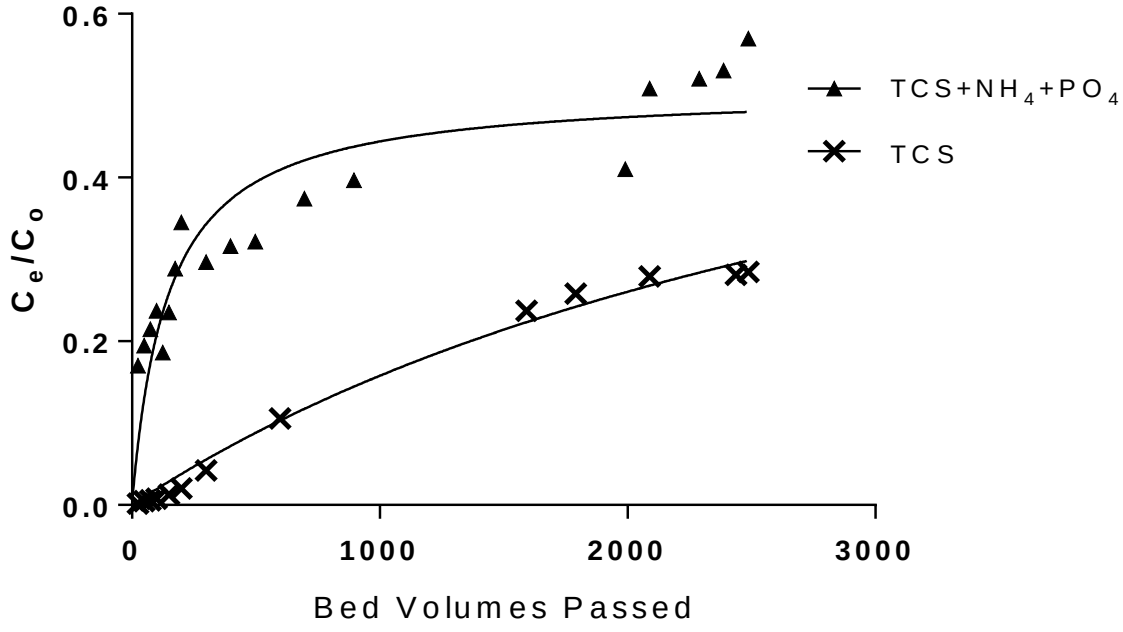

Figure 4.4. Impact of inorganic nutrient competition on triclosan removal. Experiments were conducted at pH 7, 10 mL/min flow rate, and 6 grams of BS-biochar adsorbent. Nutrients were added to solution at concentrations of approximately 1 mg/L as PO_4-P and 50 mg/L as NH_3-N. TCS was added to Milli-Q water solutions at approximately 350 µg/L.

Note: For clarity, maximum value shown on y-axis for C_e/C_o is 0.6, rather than 1.0 as shown in previous figures.

Biochar in the presence of nutrients removed over 450 µg/g BS-biochar after 2,000 bed volumes treated, while biochar in Milli-Q water with only TCS removed 1.33 mg/g. Corresponding C_e/C_o max values of 0.51 (R^2= 0.81) for TCS with inorganic nutrients and 0.75 (R^2= 0.99) for TCS only, which indicates suppressed adsorptive capacity for TCS in the presence of inorganic nutrients and poorer fit to the model as inorganic nutrient ions interfered with TCS adsorption to BS-biochar. Corresponding Kc values were 144 bed volumes for TCS with nutrients compared to 3,711 bed volumes for the single solute test. The Kc value was effectively reduced with the co-presence of inorganic nutrients in

solution, which indicates significantly shorter column operation time to reach saturation of the BS-biochar filter bed.

Previous research has demonstrated the ability of biochars from various feedstocks to adsorb nutrients such as phosphate and ammonium from water and wastewater solutions (Cao and Harris 2010; Reddy et al. 2014; Ulrich et al. 2015). In particular, recent research has demonstrated the ability of biosolids-derived biochar to adsorb up to 5.8 mg/g NH_3-N from aqueous solutions (D E Carey, McNamara, and Zitomer 2013), but was conducted with biochar activated with a KOH solution compared to biochar activation with HCl in this study. Similarly, biochar derived from anaerobically digested sugar beet tailings has demonstrated removal of over 73% of phosphate from aqueous solutions (Yao et al. 2011). In the current study, the removal of TCS was suppressed due to the co-presence of NH_4^+ and PO_4^{3-} ions in solution, however, the BS-biochar did not exhibit a strong affinity for adsorption of these ionic nutrient compounds during adsorption experiments, as demonstrated in Figure 4.5.

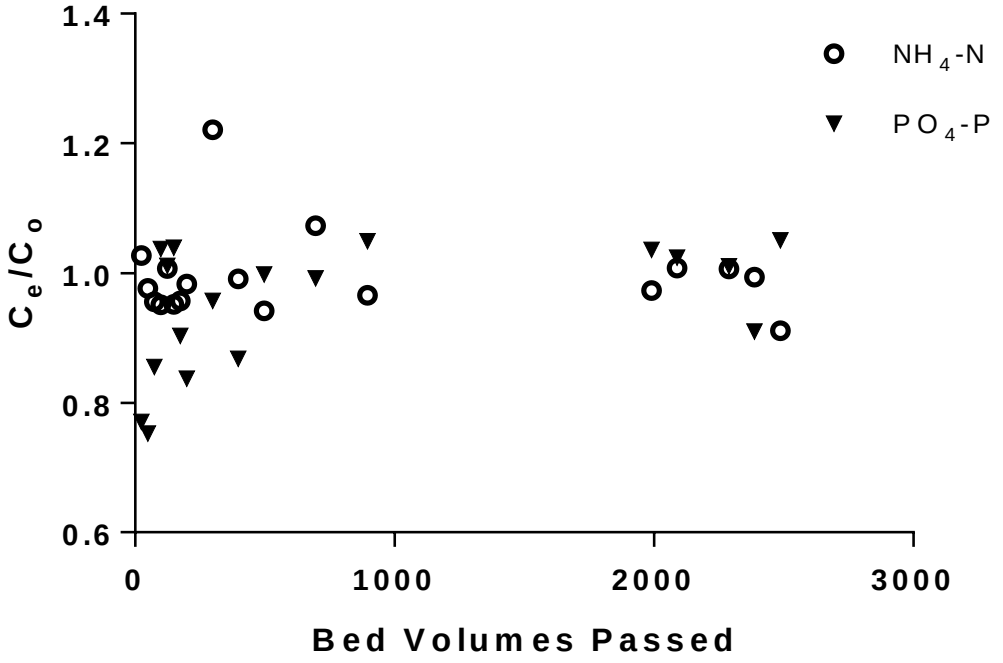

Figure 4.5. Removal of inorganic nutrients using biosolids-derived biochar. Experiments were conducted at pH 7, 10 mL/min flow rate, and 6 grams of BS-biochar adsorbent. Nutrients were added to solution at concentrations of approximately 1 mg/L as PO_4-P and 50 mg/L as NH_3-N. TCS was added to Milli-Q water solutions at approximately 350 µg/L. Ammonium was measured as NH_4-N, and phosphate as PO_4-P.

Note: For clarity, y-axis values range from 0.6 to 1.4 for C_e/C_o.

Poor removal performance of inorganic nutrients in this study, especially phosphate, in comparison to TCS may be attributed to relatively slow adsorption kinetics associated with phosphate removal via biochar from aqueous solutions. For example, engineered biochar prepared from Mg-enriched tomato tissues (e.g. tomato plant leaves) exhibited maximum adsorptive capacities over 100 mg/g for phosphate, but slow kinetic rates were observed for adsorption (Yao et al. 2013). Inorganic nutrient ions in this study may not have effectively adsorbed to BS-biochar in continuous flow-through columns, but reduced TCS adsorption. The reduction in TCS sorption could be attributed to the

physical blocking of surface adsorption sites by the nutrient ions coexisting in solution. Nutrients in solution were present at much higher concentrations compared to TCS, and likely contributed to interference between molecular interactions between TCS molecules and adsorption sites on the BS-biochar surface. Furthermore, C_e/C_o values greater than 1 were observed for nutrients in this study, which may suggest the potential for nutrients to leach from the BS-biochar during filtration. Prior to implementation at WWRFs, future research should be conducted with BS-biochar in continuous flow-through columns to determine if nutrients are adsorbed or released during treatment.

4.5 Impact of Secondary Wastewater Matrix on Triclosan Removal

Triclosan removal was hindered in wastewater relative to Milli-Q water (Figure 4.6). Mass breakthrough of TCS in column effluent during wastewater experiments was observed after 620 bed volumes, compared to 723 bed volumes in Milli-Q water. Corresponding EBCT values for the wastewater adsorption experiments and Milli-Q experiments were 1.2 minutes. The mass of TCS removed after 2,000 bed volumes in the wastewater adsorption experiment was 667 µg/g, compared to 1.33 mg/g for Milli-Q experiments. Corresponding C_e/C_o max values of 0.78 (R^2= 0.99) for TCS removal from wastewater, compared to 0.74 (R^2= 0.99) for TCS removal from Milli-Q via BS-biochar. These values suggest that the overall adsorptive capacity of TCS is not significantly less in wastewater compared to Milli-Q, but that the kinetic rates associated with TCS adsorption to BS-biochar are reduced. This reduction in TCS removal is illustrated in Figure 4.6 by the sharper rise in the breakthrough curve for wastewater compared to Milli-Q. Furthermore, corresponding Kc values for TCS removal from wastewater were 828 bed volumes, compared to 3,711 for TCS removal from Milli-Q. The larger Kc

value for TCS removal from Milli-Q water suggests that significantly more bed volumes could be treated prior to reaching exhaustion of the BS-biochar filter bed, presumably due to the lack of organic matter compared to wastewater effluent.

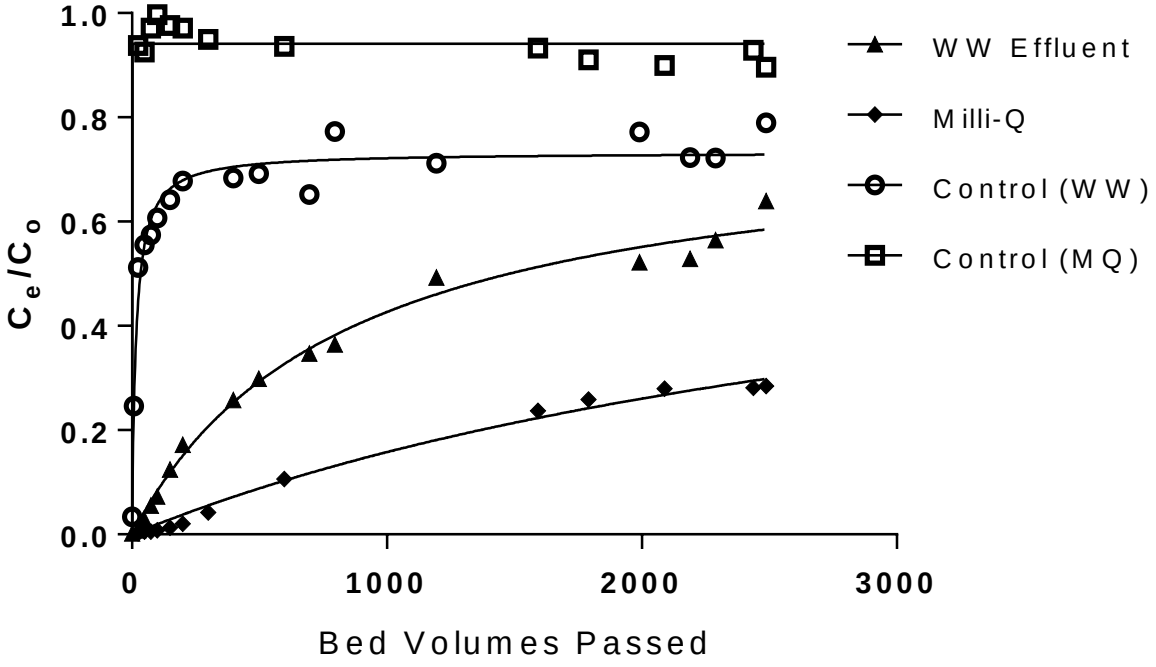

Figure 4.6. Impact of secondary wastewater matrix on TCS removal. Experiments were conducted with a flow rate of 10 mL/min and BS-biochar columns were packed with 6 g adsorbent. Control columns were packed with only glass beads and no adsorbent. TCS stock solution was added to wastewater effluent at approximately 500 ug/L. The background triclosan concentration in the secondary wastewater effluent was below detection limit (2 µg/L).

The presence of organic matter and other constituents in secondary wastewater effluent decreased the removal of TCS. Wastewater characteristics for influent secondary effluent wastewater used in adsorption experiments are shown in Table 4.5. Additional wastewater characteristics presented in Appendix A include Table A1: Solids Analysis for Secondary Wastewater Effluent Test 1, Table A2: Solids Analysis for Secondary

Wastewater Effluent Test 2, and Table A3: Column Influent and Effluent Water Quality Measurements (e.g. pH and conductivity).

Additionally, the breakthrough curve of the control experiment indicates a fraction of hydrophobic TCS molecules can be removed from wastewater through surface adsorption to wastewater solids themselves, which accumulated in the columns during operation. This TCS removal mechanism was expected due to numerous studies that have reported adsorption of TCS to organic matter and subsequent aqueous phase removal in wastewater treatment processes such as activated sludge (Bester 2003; Heidler and Halden 2007; Lozano et al. 2013; McAvoy et al. 2002; Singer et al. 2002).

Table 4.5. Characterization of Secondary Wastewater Effluent Water Quality

	pH	COD (mg/L)	TOC (mg/L)	Background TCS Conc. (µg/L)	PO_4-P (mg/L)	NH_3-N (mg/L)
WW Test 1	7.25	24.1	48.2	< 2	< 0.15	< 0.5
WW Test 2	7.20	25.7	52.7	< 2	< 0.15	< 0.5

Note: Test 1 was conducted with BS-biochar and control columns, and test 2 was conducted with BN-biochar and CF300-AC.

Previous studies have suggested that the presence of organic matter along with trace organic contaminants in influent water causes competitive adsorption effects, including direct site competition and pore blockage, which can fluctuate with varying levels of organic matter (Behera, Oh, and Park 2010; Tan et al. 2015; Uchimiya et al. 2010). Direct site competition is considered to be the strongest effect of organic matter competition because it reduces the equilibrium capacity of adsorption sites for trace organic compounds (Schindeman et al. 2012; Oleszczuk et al. 2012; Yu, Peldszus, and Huck 2009). Direct competition for adsorption sites is thought to occur primarily in

small micropores of adsorbents where trace organics preferentially adsorb and can be blocked by NOM molecules small enough to access these adsorption sites (Agrafioti et al. 2013; Chingombe, Saha, and Wakeman 2005; Qian et al. 2015). Similarly, pore blockage, or pore constriction, has been previously documented in studies where organic matter competition reduced the intraparticle adsorption kinetic rates of trace organic compounds to biochar (Ahmad et al. 2014; J. Chen, Zhu, and Sun 2007; Ulrich et al. 2015; Shimabuku et al. 2016; Yu, Peldszus, and Huck 2009; Oh and Seo 2015). This competition mechanism results from larger organic particles that cannot directly access small micropore sites, but can effectively block internal adsorption pathways that aid in adsorption of smaller trace organic compounds (Jung et al. 2013; Kong et al. 2011; Mohan et al. 2014).

Organic matter in column adsorption experiments not only affected the rate of TCS adsorption to BS-biochar in the current study, but also accumulated to the point where the volumetric flow rate of wastewater was restricted in the continuous flow-through column. This effect was observed after approximately 2,500 bed volumes of operation for the wastewater column tests conducted (see photographs of organic matter accumulation in column tests in Appendix B). For practical applications, the biochar filter would need to be backwashed to remove surficial accumulation of organic matter upon reaching this point. Further research using BS-biochar as an adsorbent in pilot-scale contactors would need to be conducted prior to full-scale implementation to determine the appropriate backwash intervals, bed service life, and other operational parameters. For any application, an appropriate balance would need be determined for specific contaminant removal criteria and desired bed service life.

4.6 Comparison of Biosolids-Derived Biochar to Commercial Adsorbents

Triclosan removal via biosolids-derived biochar produced in this study was compared to two commercial adsorbents made from different feedstocks. The GAC used in adsorption experiments (Calgon Filtrasorb® 300, CF300-AC) is commonly used for the removal of dissolved organic compounds from water and wastewater. This activated carbon product is produced from select grades of bituminous coal through a process known as reagglomeration, which involves pulverizing and crushing coal briquettes to achieve a desired particle size. This process also produces more homogenous pore structures that are better for certain organic contaminant removal (Schindeman et al. 2012). Additionally, a commercially sold biochar product made from pine-wood (Biochar Now, BN-biochar) was used to compare TCS adsorption with different types of biochars in continuous flow-through columns. The BN-biochar is produced through slow pyrolysis in an oxygen-depleted environment, comparable to the BS-biochar produced in this study.

4.6.1 Physical Characteristics of Adsorbents

Surface morphology and physical characteristics of adsorbents were analyzed through BET surface area analysis, SEM imaging, and FTIR analysis. The results of the surface area analysis including total BET surface area (m^2/g), total pore volume (cm^3/g), total micropore volume (cm^3/g), and average pore radius (Å) are included in Table 4.6. The results from the physical characterization of adsorbents indicate that the CF300-AC has the highest overall surface area, total pore volume, and total micropore volume compared to BS-biochar and BN-biochar. The BS-biochar produced in this study was pyrolyzed at 600°C in a muffle furnace, and the BN-biochar is commercially produced by

slow pyrolysis in a kiln-based technology that can achieve temperatures above 600°C. Previous studies have demonstrated that higher pyrolysis temperatures, or activation temperatures, are positively correlated with increases in biochar surface area (T. Chen et al. 2014; Hossain et al. 2011; Lu et al. 2013). Higher production temperatures can increase porosity of biochar, but the overall yield of biochar produced decreases with elevated pyrolysis temperatures (T. Chen et al. 2014; Hadi et al. 2015; Lu et al. 2013; Smith et al. 2009). In addition, biosolids-derived biochar adsorbents can be modified through a variety of chemical activation methods to increase the specific surface area, such as through KOH activation (1,686 m^2/g) (Ros et al. 2006) and $ZnCl_2$ activation (450 m^2/g) (Yu and Zhong 2006), compared to HCl activation used in this study. For a particular application, the production process could be modified to produce biochar adsorbents that are tailored to maximize desired attributes, such as surface area and porosity, while considering chemical costs associated with activation processes.

Table 4.6. Physical characteristics of adsorbents.

Adsorbent	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Radius (Å)	Total Micropore Volume (cm^3/g)
BS-biochar	182	0.0874	2.83	0.0778
BN-biochar	44	0.0229	1.88	0.0184
CF300-AC	698	0.3217	4.64	0.3208

The surface morphology for each adsorbent used in column adsorption experiments was visualized using SEM imaging (Figure 4.7). The CF300-AC appeared to be more porous compared to the BS-biochar and BN-biochar. Additionally, the pore structure of the BS-biochar produced in this study appears to be more heterogeneous compared to BN-biochar, but lacks the larger pores as shown on the CF300-AC. The large pores and

highly irregular surface morphology of the activated carbon are characteristic of coal-derived carbonaceous adsorbents, which are typically produced through energy-intensive thermal activation processes including high temperatures and steam (Thompson et al. 2016; Bhatnagar et al. 2013). The increased number of irregular surfaces and larger pores on the activated carbon surface increased the specific surface area, thus increasing the adsorption capacity for TCS.

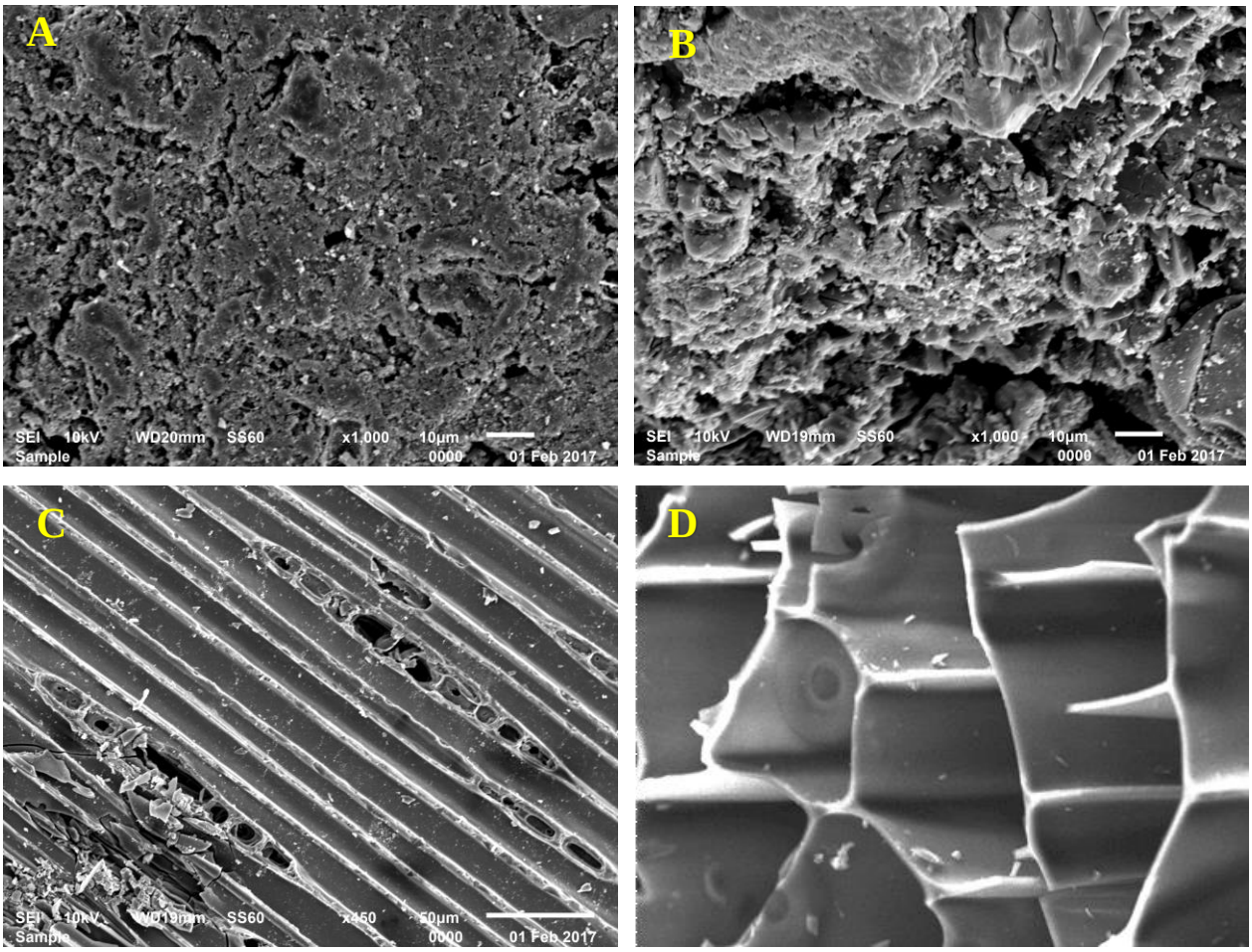

Figure 4.7. Scanning electron microscope images of adsorbents. (a) BS-biochar, (b) CF300-AC, and (c, d) BN-biochar. (a) and (b) are at 1000x magnification, (c) is shown at 450x, and (d) is shown at 1200x for clarity.

Note: Image (d) of BN-biochar was taken from the manufacturer's webpage: (BiocharNow 2017).

FTIR analysis was used to elucidate functional groups present on the surface of the adsorbents used in this study (Appendix C). Previous research has suggested that biosolids-derived biochar (similar to the BS-biochar produced in this study) contains C-O bonds on the biochar surface, such as in phenols, esters, and carboxylic functional groups (Méndez et al. 2005; Tong, Mayer, and McNamara 2016). Similarly, the BS-biochar produced in this study appears to have a broad band present at 1200 cm^{-1}, which is associated with C-O bonds present in oxygen-containing functional groups. Polar oxygen-containing functional groups such as carboxyl and phenol groups likely interact with phenyl groups on TCS molecules via hydrogen bonding, and aromatic groups present on both the adsorbent and adsorbate surface may also contribute to π- π stacking (Lei, Hu, and He 2013; Tong, Mayer, and McNamara 2016). The CF300-AC and BN-biochar FTIR spectra each contain broad peaks around 600 cm^{-1}, but do not have peaks corresponding to the 1200 cm^{-1} wavenumber. Additionally, the BS-biochar and BN-biochar have broad bands present at 1700 cm-1, which may be associated with C=O stretching in lactones and carboxylic anhydrides (Méndez et al. 2005).

4.6.2 Impact of Adsorbent Material on Triclosan Removal

The removal of TCS from Milli-Q water was compared for CF300-AC, BS-biochar, and BN-biochar. Mass breakthrough of TCS was observed in column effluent after 219 bed volumes for BN-biochar, compared to 780 and 1,404 bed volumes for BS-biochar and CF300-AC, respectively (Figure 4.8). The mass of TCS removed after 2,000 bed volumes treated with BS-biochar was 1.33 mg/g, compared to 1.40 mg/g for CF300-AC and 280 µg/g for BN-biochar. Corresponding C_e/C_o max values of 0.12 (R^2= 0.92) for CF300-AC, 0.59 (R^2= 0.98) for BS-biochar, and 0.89 (R^2= 0.98) for BN-biochar.

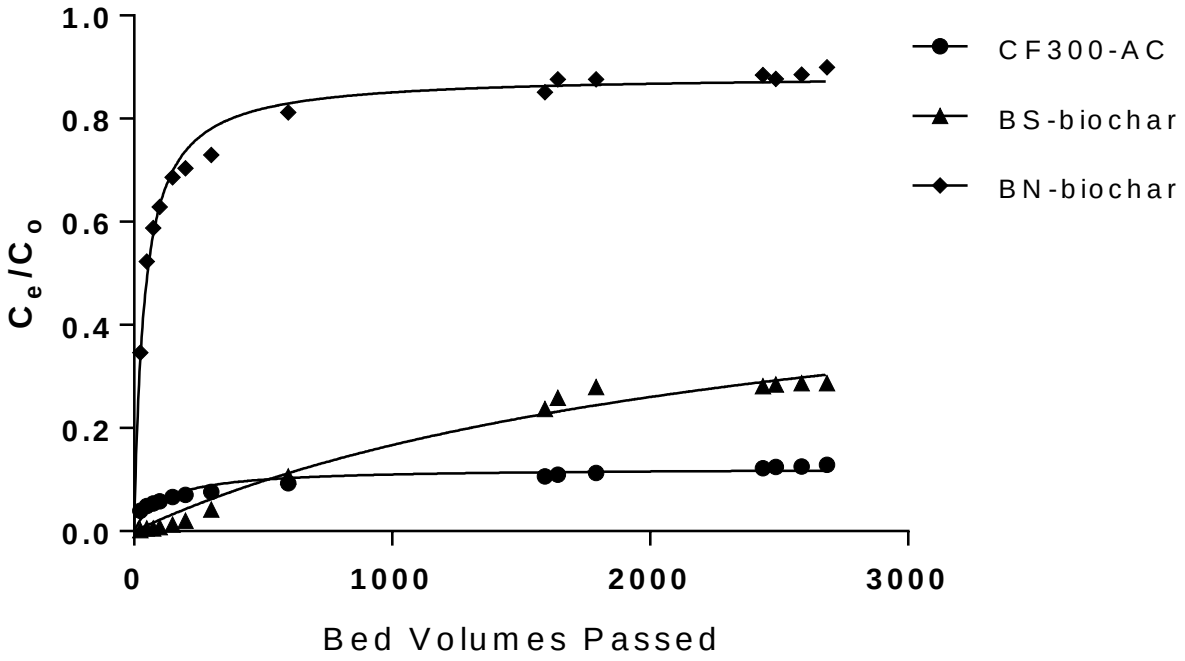

Figure 4.8. Impact of adsorbent material on triclosan removal from Milli-Q water. Experiments were conducted at pH 7 with a flow rate of 10 mL/min. 5" of each adsorbent was packed into glass columns to obtain similar EBCT values. TCS was added to Milli-Q water at approximately 500 µg/L.

The breakthrough curves and C_e/C_o max values suggest that the CF300-AC adsorptive capacity for TCS was not approached, and agrees with previous results from batch equilibrium experiments where over 250 mg/g TCS was sorbed to activated carbon (Fang, Pendleton, and Badalyan 2009; Oh and Seo 2015). The removal of TCS through adsorption to BN-biochar was markedly worse in comparison to the BS-biochar and CF300-AC, which is likely related to the smaller surface area and pore volume. Corresponding Kc values for TCS removal were 112 bed volumes for CF300-AC, compared to 40 bed volumes for BN-biochar, and 2,539 bed volumes for BS-biochar. These results indicate that BN-biochar reached saturation after much fewer bed volumes treated as compared to CF300-AC and BS-biochar. The small Kc value for CF300-AC

implies that C_e/C_o max was rapidly reached, however, TCS removal plateaued around approximately 90% removal, which was the highest observed TCS removal during Milli-Q experiments. BS-biochar had the highest observed Kc value in this study, but demonstrated lower adsorptive capacity for TCS compared to CF300-AC.

The removal of TCS from secondary wastewater effluent was investigated using CF300-AC, BN-biochar, and BS-biochar adsorbents. Municipal secondary wastewater effluent was obtained from the Jones Island Water Reclamation Facility in Milwaukee, WI. Mass breakthrough of TCS was observed in column effluent after 250 bed volumes for BN-biochar, compared to 498 and 1,643 for BS-biochar and CF300-AC, respectively (Figure 4.9).

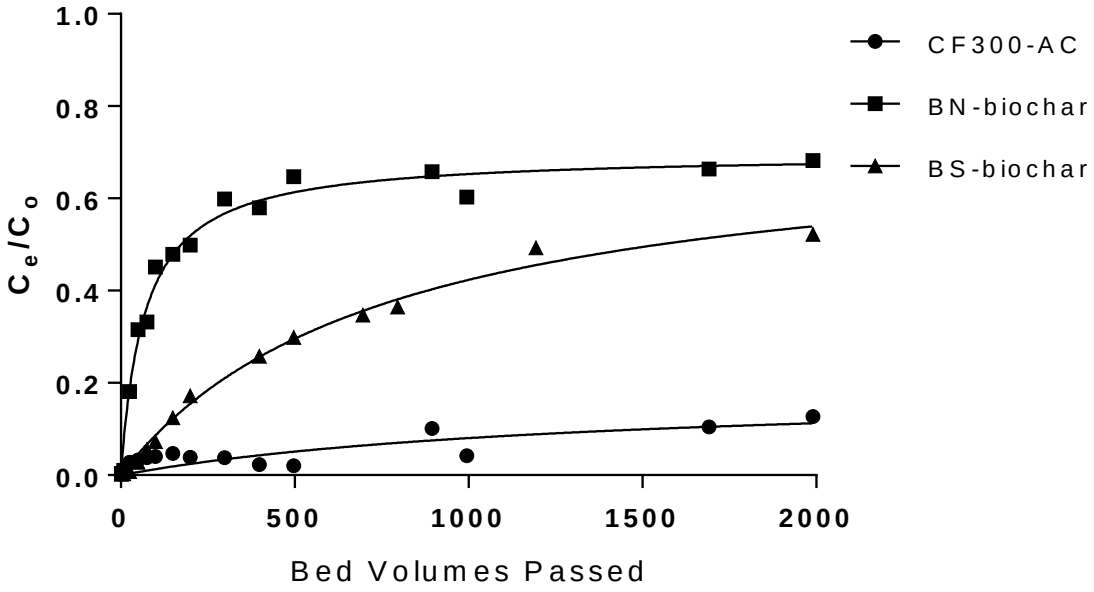

Figure 4.9. Impact of adsorbent material on triclosan removal from secondary wastewater effluent. Experiments were conducted at pH 7 with a flow rate of 10 mL/min. 5" of each adsorbent was packed into glass columns to obtain similar EBCT values. TCS was added to secondary wastewater effluent at approximately 500 µg/L.

The mass of TCS removed after 2,000 bed volumes treated with BS-biochar was 667 µg/g, compared to 520 µg/g for BN-biochar and 1.07 mg/g for CF300-AC. TCS removal via BS-biochar was reduced by 50% in secondary effluent compared to removal from Milli-Q water, while TCS removal with CF300-AC decreased by approximately 25%. TCS removal from wastewater with BN-biochar increased by 86% compared to Milli-Q water, and resulted in an increase in bed volumes treated prior to mass breakthrough in column effluent. Corresponding C_e/C_o max values of 0.75 for BS-biochar (R^2= 0.98), compared to 0.70 for BN-biochar (R^2= 0.99) and 0.19 for CF300-AC (R^2= 0.58).

The results from wastewater adsorption experiments indicate that TCS is removed from wastewater much more efficiently with CF300-AC compared to BS-biochar and BN-biochar. The low C_e/C_o max value and poor model fit for CF300-AC suggests that the TCS adsorptive capacity was not approached, which was demonstrated by the suppressed breakthrough curve. C_e/C_o max values for BS-biochar and BN-biochar were similar for wastewater experiments. However, the BS-biochar demonstrated consistently higher removal rates and slower saturation of adsorption sites compared to BN-biochar. Similarly, corresponding Kc values of 762 bed volumes for BS-biochar compared to 69 bed volumes for BN-biochar suggest that significantly more bed volumes can be treated with BS-biochar prior to reaching saturation. The highest observed Kc value of 1,340 bed volumes was determined for CF300-AC, and indicates that an increased number of bed volumes can be treated prior to reaching saturation of the adsorbent.

4.7 Extended Duration Column Study to Approach Exhaustion

An extended duration column adsorption experiment was conducted to determine the overall TCS adsorption capacity for BS-biochar. The goal of the experiment was to determine the number of bed volumes at which TCS removal via BS-biochar would be reduced below 95% C_e/C_o, at which point the filter bed is considered exhausted. The TCS adsorption experiment was conducted for 3 weeks, and treated over 42,000 bed volumes while still maintaining approximately 50% TCS removal, as shown in Figure 4.10.

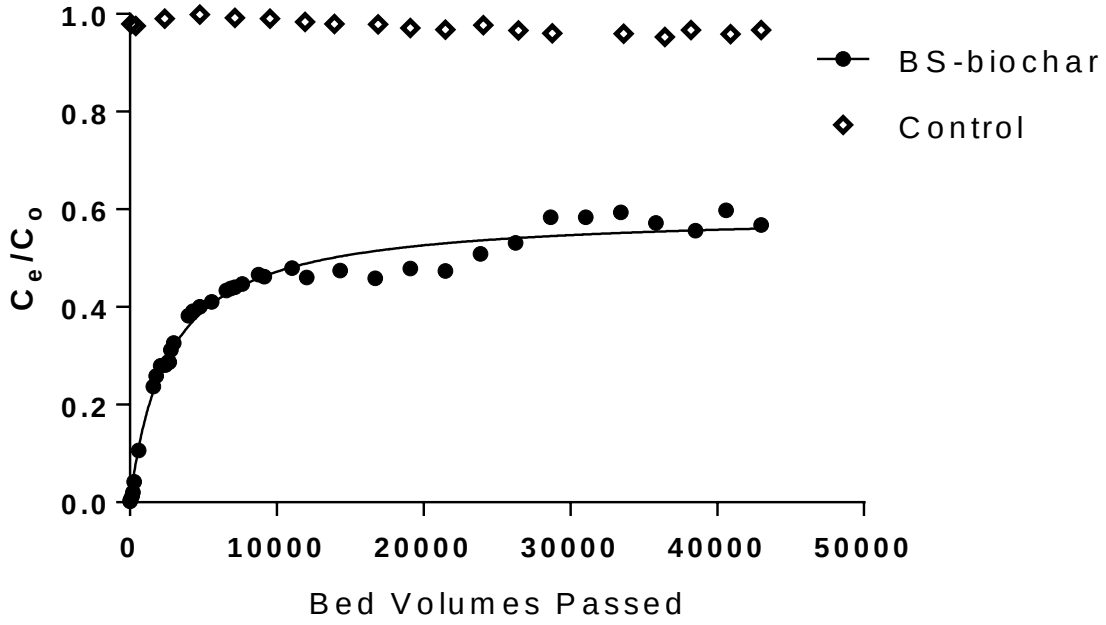

Figure 4.10. Triclosan removal via biosolids-derived biochar. The extended duration column test was conducted at pH 7, 10 mL/min, and 6 g of BS-biochar adsorbent. The control column duplicated the BS-biochar experiment with no biochar adsorbent packed into the column. TCS was added to Milli-Q water at approximately 700 µg/L.

Exhaustion of the BS-biochar adsorbent was not achieved in the experiment, although mass breakthrough of TCS in column effluent was observed after 6,632 bed volumes. The mass of TCS removed after 2,000 bed volumes was 1.53 mg/g, and BS-

biochar removed over 15.8 mg/g after 42,000 bed volumes treated. Non-linear analysis yielded a C_e/C_o max value of 0.59 for BS-biochar (R^2= 0.99) and a Kc value of 2,586 bed volumes. These results indicate that TCS removal plateaued around 40% with the BS-biochar sorbent, and did not approach exhaustion during the experiment. The column adsorption experiment was discontinued after the TCS removal remained constant (within 5%) for the final 15,000 bed volumes treated prior to the completion of the test. Future research could increase initial TCS concentration and decrease BS-biochar adsorbent mass to try to approach exhaustion, however, this adsorption capacity would never be approached in real-world wastewater streams where other organic micropollutants, nutrients, and organic matter would be present in solution. Additionally, the water solubility of TCS at 25°C ranges from 1.97 to 4.6 mg/L, therefore limiting the amount of TCS that can be added to water and wastewater for adsorption testing (Halden and Paull 2005).

4.8 Environmental Implications

During the past century, the quantity of sludge produced from municipal WRRFs has increased greatly due to industrialization and urbanization (Lozano et al. 2012; Smith et al. 2009). Disposal of sludge and biosolids in landfills is a common practice because of its ease and low cost, but is not a sustainable method of disposal due to concerns related to pollution and lack of material recovery (Hadi et al. 2015). In recent years, modification and reuse of biosolids as a valuable adsorbent for the removal of contaminants has emerged as one of the most popular techniques for sludge processing for beneficial reuse (Agrafioti et al. 2013; Inyang and Dickenson 2015; Tong, Mayer, and McNamara 2016; Qian et al. 2015; Xie et al. 2015). Implementing biosolids reuse

practices, such as producing adsorbents, could provide multiple benefits to WRRFs through minimization of biosolids sent to landfills for disposal and increased removal of contaminants prior to discharge to receiving waters.

Implementation of biochar as a tertiary wastewater treatment process could help mitigate the amount of organic micropollutants and other unregulated contaminants that are discharged to the environment from WRRF effluents. The presence of organic micropollutants in freshwater ecosystems poses significant ecological risks to aquatic species such as fish, algae, and invertebrates (Fritsch et al. 2013; Kidd et al. 2007; Orvos et al. 2002). Developing sustainable treatment technologies that enhance the removal of organic micropollutants should be considered of high importance for WRRFs, especially in areas where receiving waters are sensitive ecosystems or have large populations downstream that rely on the same sources of water for potable water supplies.

Previous research has demonstrated that the spent BS-biochar adsorbent material could be re-pyrolyzed to remove micropollutants such as triclosan, triclocarban, and nonylphenol after use (Ross et al. 2016). The re-pyrolyzed BS-biochar material could then be reused as an adsorbent for several cycles until significant degradation to the physical structure prevented effective use as an adsorbent. Following use as an adsorbent, the BS-biochar could be pyrolyzed to remove remaining microconstituents and land applied as a soil amendment, where numerous studies have documented the positive impact of biochar on carbon sequestration and nutrient holding capacity (Lehmann, Gaunt, and Rondon 2006; Inyang and Dickenson 2015).

5 CONCLUSIONS

5.1 Key Findings

The goal of this research was to determine the ability of biosolids-derived biochar to sorb triclosan from wastewater in continuous flow-through columns. TCS was selected as a representative micropollutant due to its prevalence in the natural environment and frequent detection in residual biosolids and liquid effluent from WRRFs. Column adsorption tests conducted with E2 and SMX indicate that BS-biochar could potentially be used to remove a variety of organic micropollutants from wastewater. The following conclusions are based on laboratory-scale column adsorption experiments.

1. Biosolids-derived biochar can remove micropollutants from water and wastewater streams in continuous flow-through columns. Results from column adsorption experiments demonstrate that BS-biochar can remove micropollutants such as E2, TCS, and SMX from water and wastewater solutions.

2. The impact of bulk solution pH on TCS removal from water was negligible in column adsorption experiments conducted at pH 7 and 8.5. BS-biochar adsorbents would most likely be employed to treat wastewater streams with near-neutral pH, and the results demonstrated the capability of BS-biochar for the removal of TCS in this pH range.

3. The impact of flow rate, or contact time, on TCS adsorption to BS-biochar was substantial. The removal of TCS from Milli-Q water solutions was highest at lower flow rates tested, and decreased with increasing flow rates (2.58 gpm/ft^2 > 5.16 gpm/ft^2 > 10.32 gpm/ft^2).

4. The presence of organic micropollutants did not significantly impact TCS removal. BS-biochar demonstrated higher affinity for hydrophobic micropollutants E2 and TCS, but also efficiently removed SMX from solution. These results add to the body of scientific knowledge supporting the use of BS-biochar as an adsorbent for the removal of a wide variety of pollutants from water and wastewater streams.

5. Inorganic nutrient competition experiments demonstrated that TCS removal decreased in the presence of inorganic nutrient ions, NH_4^+ and PO_4^{3-}. BS-biochar did not efficiently remove inorganic nutrients from solution, but rates of TCS adsorption decreased with the co-presence of inorganic nutrient ions compared to single solute experiments.

6. TCS removal from secondary wastewater effluent via BS-biochar was lower compared to Milli-Q water experiments. The reduction in TCS adsorption was attributed to the competition of organic matter and other wastewater constituents for adsorption sites on the BS-biochar.

7. Activated carbon (CF300-AC) demonstrated higher TCS adsorption capacity compared to BS-biochar, but BS-biochar was superior to pine-wood biochar (BN-biochar). Higher TCS adsorption was positively correlated with higher BET surface area and total pore volume for adsorbents.

In summary, BS-biochar adsorbents can reduce the spread of micropollutants into the environment prior to discharge of wastewater effluents to receiving waters. Additionally, the production of BS-biochar adsorbents could provide a viable biosolids management alternative to land application or incineration.

5.2 Future Research

Future research should be conducted using BS-biochar adsorbents in pilot-scale contactors to determine the feasibility of implementing BS-biochar filtration processes as a tertiary treatment technology for WRRFs. Furthermore, extensive studies of constituents present in BS-biochar filter effluent should be conducted to determine the potential for release of compounds such as nutrients and heavy metals. Preliminary data obtained from this study suggests that the BS-biochar effluent does not contain significant concentrations of harmful heavy metal compounds or nutrients, but further testing would be necessary prior to full-scale implementation in order to validate the findings in this study.

5.3 Next Steps Towards Implementation at WRRFs

Next steps towards implementation of biosolids-derived biochar adsorbents as tertiary treatment processes at municipal WRRFs include additional testing with specific wastewater streams to be treated, along with pilot-scale reactor design and subsequent

testing. Establishing desired operational parameters such as the flow of wastewater to be treated, adsorbent dosage, EBCT, and effluent water quality requirements is needed for any particular application. Contactors similar to commercial GAC configurations could be employed as side-stream tertiary treatment processes at WRRFs, configured to treat anaerobic bioreactor effluent, or used to treat industrial wastewater flows to remove specific contaminants.

Production of BS-biochar through pyrolysis of dried wastewater biosolids has previously shown the potential to generate significant amounts of energy through the co-production of py-oil and py-gas, which can be used to power boilers and combustion engines (Lehmann, Gaunt, and Rondon 2006; McNamara et al. 2016). WRRFs could simultaneously reduce costs associated with sludge disposal, produce valuable adsorbents made from biosolids, and mitigate the discharge of organic micropollutants to the natural environment through the implementation of pyrolysis and biochar production. Furthermore, for biosolids management strategies to be sustainable, simultaneous energy capture and nutrient recovery should be maximized while minimizing the impacts associated with micropollutants in the natural environment.

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APPENDIX

A: Water Quality Characteristics for Secondary Wastewater Effluent

Table A1: Solids Analysis for Secondary Wastewater Effluent Test 1

Replicate	TS	VS	FS	TSS	VSS	FSS	TDS	VDS	FDS
1	932	248	684	28	16	12	902	88	814
2	932	204	728	34	28	6	934	100	834
3	920	236	684	34	24	10	888	94	794
Mean	928	229	699	32	23	9	908	94	814
SD	7	23	25	3	6	3	24	6	20

All values in mg/L

Table A2: Solids Analysis for Secondary Wastewater Effluent Test 2

Replicate	TS	VS	FS	TSS	VSS	FSS	TDS	VDS	FDS
1	984	112	872	24	8	16	1036	72	964
2	996	132	864	24	12	12	1016	52	964
3	984	104	880	20	12	8	980	34	946
Mean	988	116	872	23	11	12	1011	53	958
SD	7	14	8	2	2	4	28	19	10

All values in mg/L

Table A3: Column Influent and Effluent Water Quality Measurements

	pH			Conductivity (mS/cm)		
	T= 0	T= 300	T= 1440	T=0	T=300	T=1440
Influent WW-1	7.24	7.25	7.30	1.558	1.561	1.562
BS-biochar effluent	6.95	7.15	7.25	1.541	1.555	1.556
Control effluent	7.18	7.22	7.27	1.555	1.556	1.561
Influent WW-2	7.25	7.29	7.31	1.669	1.708	1.722
BN-biochar effluent	7.10	7.13	7.23	1.720	1.738	1.774
CF300-AC effluent	7.82	7.31	7.35	1.667	1.759	1.755

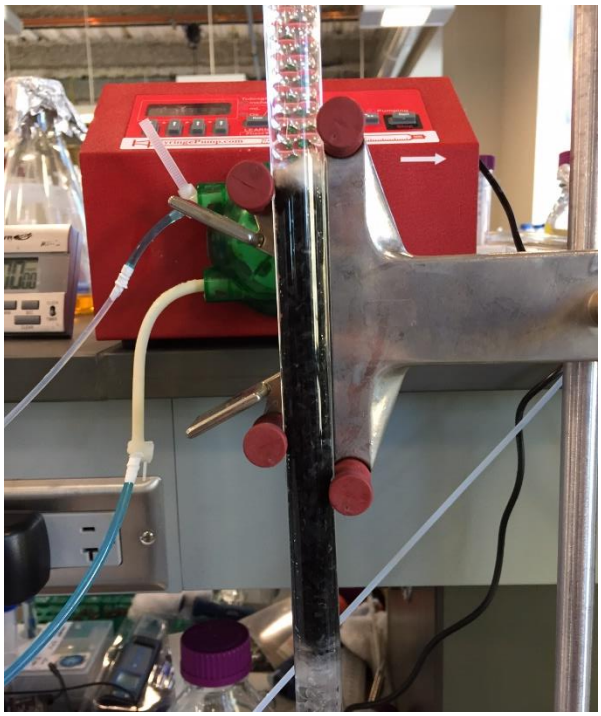
B: Photographs of the Accumulation of Organic Matter During Column Adsorption Experiments

Photograph B1:

Glass column packed with BS-biochar adsorbent at the beginning of the wastewater experiment (T= 0).

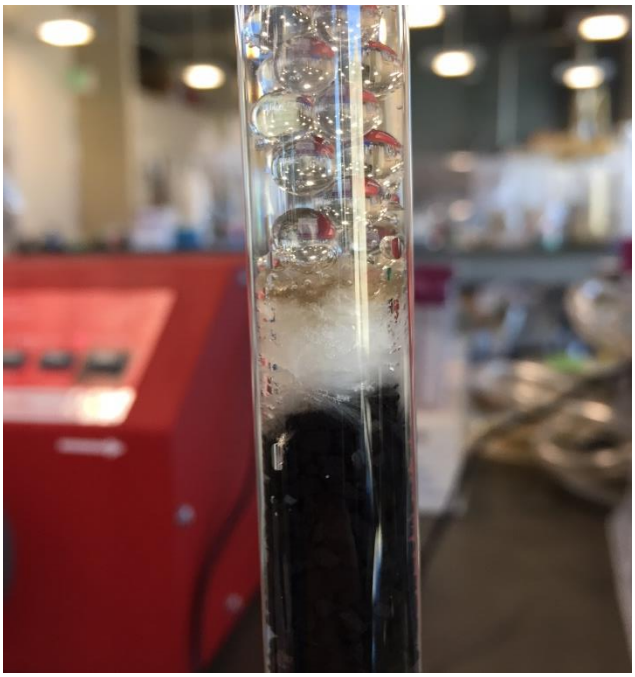
Photograph B2:

Accumulation of organic matter after 30 minutes of column operation (T= 30). Slight discoloration of top layer of glass wool can be observed.



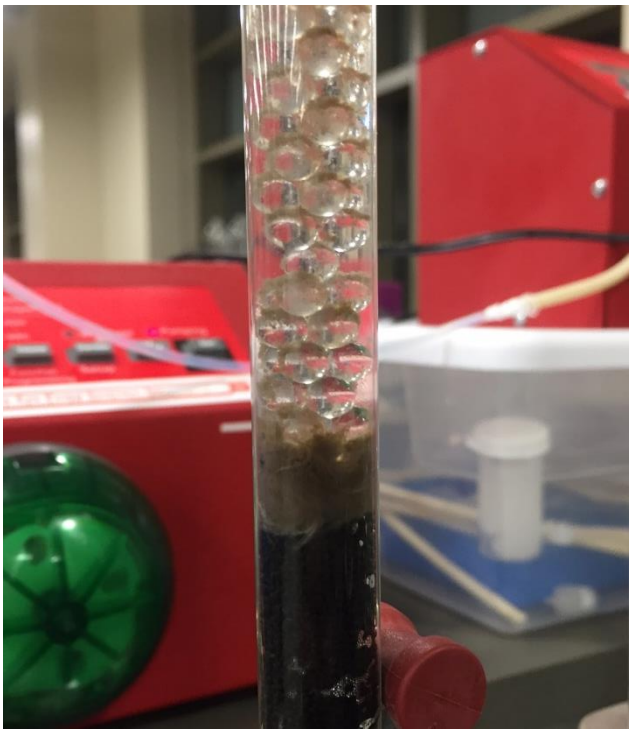
Photograph B3:

Accumulation of organic matter after 300 minutes of column operation (T= 300). A thin layer solids can be observed on top of the glass wool, which has begun to turn darker brown in color.



Photograph B4:

Accumulation of organic matter after 1,440 minutes of column operation (T= 1440). A thick layer of solids can be observed on the glass beads and glass wool, which contributed to flow rate reduction.



C: Fourier Transform Infrared Spectroscopy (FTIR) Spectra

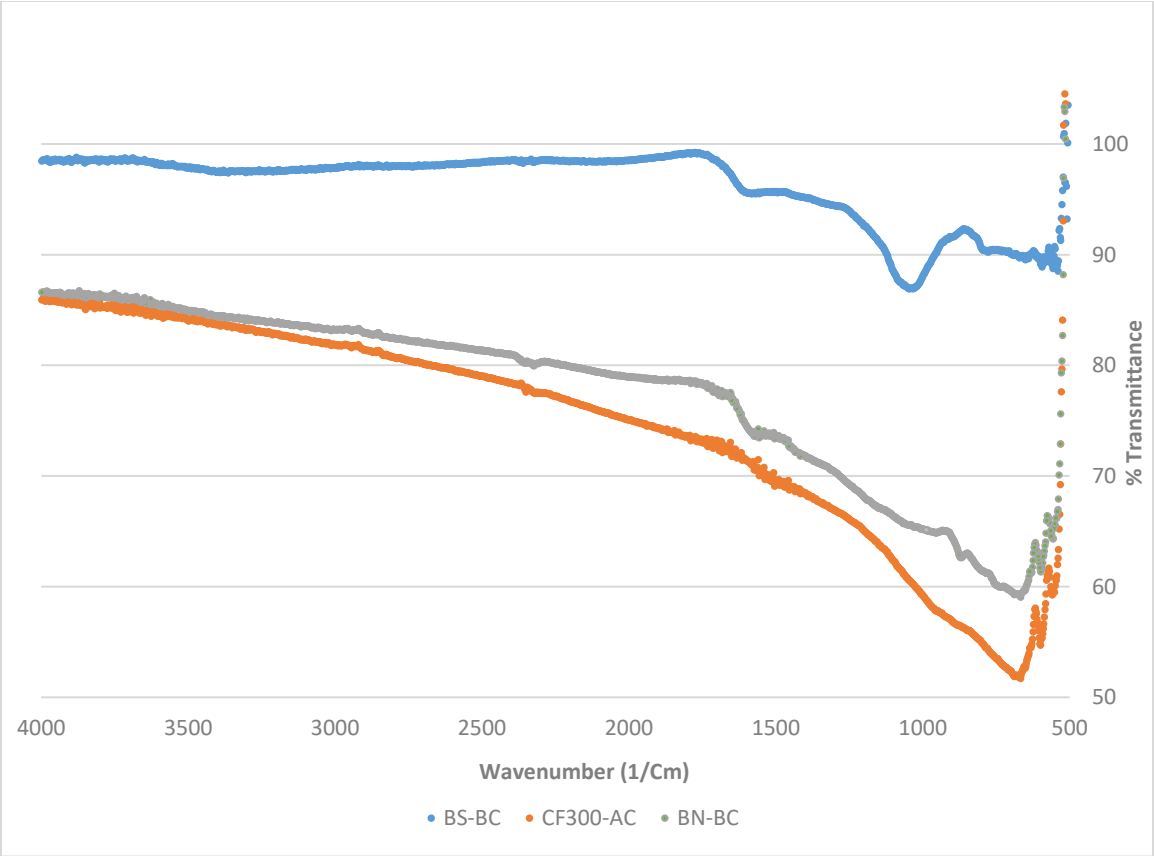


Figure C1: FTIR spectra for adsorbents used in column adsorption experiments.